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THE ELEMENTS
OF
FRACTIONAL DISTILLATION

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The late Dr. H. P. Talbot was Consulting Editor of the International Chemical Series from its inception in 1911 until his death in 1927.

THE ELEMENTS
OF
FRACTIONAL DISTILLATION

BY

CLARK SHOVE ROBINSON
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OF TECHNOLOGY, FORMERLY CHEMICAL ENGINEER WITH THE
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PREFACE

The subject of Fractional Distillation has received but scant attention from writers in the English language since Sidney Young published his book of that name in 1903 (London). French and German authors have, on the other hand, produced a number of books on the subject, among the more important of which are the following:

"La Rectification et les Colonnes Rectificatrices en Distillerie." E. Barbet, Paris (1890). 2nd Ed. (1895).

"Der Wirkungsweise der Rectificir—und Destillir—Apparate." E. Hausbrand, Berlin (1893) 3rd Ed. (1916).

"Theorie der Verdampfung und Verflüssung von Gemischen und der Fraktionierten Destillation." J. P. Kuenen, Leipzig (1906).

"Theorie der Gewinnung und Trennung der Ätherischen Öle durch Destillation." C. von Rechenberg, Leipzig (1910).

"La Distillation Fractionée et la Rectification." Charles Mariller, Paris (1917).

"Young's "Fractional Distillation," while a model for its kind, has to do almost entirely with the aspects of the subject as viewed from the chemical laboratory, and there has been literally no work in English available for the engineer and plant operator, dealing with the applications of the laboratory processes to the plant.

The use of the modern types of distilling equipment is growing at a very rapid rate. Manufacturers of chemicals are learning that they must refine their products in order to market them successfully, and it is often true that fractional distillation offers the most available if not the only way of accomplishing this. There has consequently arisen a wide demand among engineers and operators for a book which will explain the principles involved in such a way that these principles can be applied to the particular problem at hand.

68854

It has therefore been the purpose of the writer of this book to attempt to explain simply yet accurately, according to the best ideas of Physical Chemistry and Chemical Engineering, the principles of fractional distillation, illustrating these principles with a few carefully selected illustrations. This book is to be regarded neither as a complete treatise nor an encyclopedia on the subject, but, as the title indicates, an introduction to its study. It will be followed by another book dealing with the general practice of fractional distilliaton and its applications to the several industries.

In general, it has been divided into five parts. The first part deals with fractional distillation from the qualitative standpoint of the Phase Rule. The second part discusses some of the quantitative aspects from the standpoint of the Chemical Engineer. Part three discusses the factors involved in the design of distilling equipment. Part four gives a few examples of modern apparatus, while the last portion includes a number of useful reference tables which have been compiled from sources mostly out of print and unavailable except in large libraries. The writer has drawn at will on the several books mentioned above, some of the tables being taken nearly bodily from them, and has also derived much help from Findlay's "Phase Rule" (London, 1920) and from "The General Principles of Chemistry" by Noyes and Sherrill (Boston, 1917). He wishes especially to express his gratitude for the inspiration and helpful suggestions from Dr. W. K. Lewis of the Massachusetts Institute of Technology, and from his other friends and associates at the Institute and of the E. B. Badger & Sons Company. Finally, he wishes to express his appreciation of the assistance of Miss Mildred B. McDonald, without which this book would never have been written.

CLARK S. ROBINSON.

CAMBRIDGE,
June 30, 1920.

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THE ELEMENTS
OF
FRACTIONAL DISTILLATION

INTRODUCTION

Definition of Fractional Distillation.—By the expression Fractional Distillation is meant the process of separating so far as it may be possible, a mixture of two or more volatile substances into its components, by causing the mixture to vaporize by suitable application of heat, condensing the vapors in such a way that fractions of varying boiling points are obtained, revaporizing these fractions and separating their vapors into similar fractions, combining fractions of similar boiling points, and repeating until the degree of separation desired is finally obtained.

Purpose of Book.—Such a process is occasionally met with in the chemical laboratory, but it is a laborious and time consuming operation that has its chief value as a problem for the student, for the purpose of familiarizing him with some of the characteristic properties of volatile substances. It is possible to carry on a fractional distillation by means of certain mechanical devices which eliminate almost all of this labor and time, and which permit separations not only equal to those obtained by this more tedious process but far surpassing it in quality and purity of product. It is the purpose of this book to indicate how such devices may be profitably used in the solution of distillation problems.

Origin of Fractional Distillation.—Like all of the older industries, fractional distillation is an art which originated in past ages, and which developed as did all the arts, by the gradual accumulation of empirical knowledge. It is probable that its growth took place along with that of the distilled alcoholic beverages, and to the average person today the word "still" is synonymous with rum, brandy, and other distilled liquors. To France, which has been the great producer of brandy, belongs the credit of the development of the modern fractionating still.

Physical Chemistry and Fractional Distillation.—Fractional distillation has labored under the same sort of burden that the other industrial arts have borne. Empirical knowledge will carry an industry to a certain point and further advances are then few and far between. It has been the function of the sciences to come to the rescue of the arts at such times and thus permit the advancement to greater usefulness. The science that has converted fractional distillation from an art to a science is Physical Chemistry. By its aid the study of fractionation problems becomes relatively simple, and it is on this account that the subject matter in this book is based upon Physical Chemistry as its foundation.

CHAPTER I

THE PHASE RULE

There is a law of thermodynamics, known as the Phase Rule, by which it is possible to predict exactly the conditions under which all systems of equilibrium can exist. This law was first stated by Gibbs,[1] and has since been applied to a very large number of equilibria. The rule is so simple and its application gives such an insight into the conditions under which a system may be in equilibrium that it will be of the greatest profit to study fractional distillation in its light.

Definition of Phases.—All systems are considered to consist of one or more separate portions, each portion being separated from the other by definite physical boundaries. For instance, in the system consisting of ice, liquid water, and water vapor, there is a sharp physical boundary between the ice and the water, a sharp boundary between the ice and the water vapor, and a boundary between the liquid and the vapor. It is said that such a system is one of three portions, or *phases*. The ice may be divided into a number of small pieces, separated from each other by liquid, but there still remains but one solid phase. Again, if a piece of iron containing 0.85 per cent carbon is allowed to cool very slowly from a high temperature and its surface is polished, etched, and examined under the microscope, the surface of the metal is found to consist of fine dark and light lines parallel to each other. The light lines consist of an iron-carbon compound called cementite, and the dark lines are pure iron. It is said, therefore, that this metal, apparently homogeneous to the eye, consists of two solid phases.

Types of Phases.—A phase, however, while it must be homogeneous physically, may consist of a number of different kinds of substances. A solution of a mixture of salt and sugar in water, consists of but one phase, although there are three separate substances present. However, if there were an excess of salt and sugar added to the water, so that the solution was unable to dissolve all of them, and some of the salt and sugar remained undissolved, the system then would have four phases—solid salt, solid sugar, the solution and the water vapor above the solution. In the same way, the vapor present in a system is always considered as one phase, since it is impossible to distinguish between the various components by any physical means.

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[1] Trans. Conn. Acad., III, pp. 108–248 (1876); pp. 343–524 (1878).

Phase Rule Qualitative Only.—It is, of course, evident that the number of phases present in a system is independent of the relative quantities of the respective phases, and, therefore, in discussing equilibrium conditions, the Phase Rule will give no insight into the quantitative relationship between the phases.

Definition of Components.—A system may consist of one or more pure components, and the maximum number of phases which may be present at equilibrium depends upon the number of components. It is, therefore, important to define what a component is. The components of a system are the *smallest number* of pure chemical substances out of which it is possible to construct the entire system. For instance, the system, ice, water and water vapor, consists of one component, the pure substance H_2O, although it is also possible to produce the system from the two elements, Hydrogen and Oxygen. In the same way, the system—solid salt, solid sugar, saturated solution and vapor, consists of three components, salt, sugar and water.

Definition of Variants.—The conditions under which a system can exist at equilibrium with respect to its various phases, are subject to a certain amount of variation. A system can be subjected to different temperatures; the pressure on the system can be varied; the concentrations of the solutions and vapors can be changed; it is possible to vary the specific gravity and the index of refraction of a solution. Not all of these changes can be made independently of each other, however, and it is customary to distinguish between such by referring to independent and dependent variations or variants, and the number of independent variations which it is possible for a system to have are termed its Degrees of Freedom.

By definition the variants of a system are any physical characteristics or conditions of the whole system or of a single phase which are independent of the amounts of the phases, and the degree of freedom are the number of variants which can be modified without necessitating the disappearance of an old phase or the appearance of a new one.

Degree of Freedom.—The variants will in this book, be confined to the temperature, pressure and concentration of the components, and the degrees of freedom which a given system can have is that number of variants which must be fixed arbitrarily in order for the system to be perfectly defined.

The Phase Rule states that if the number of components of a system be called C, the degrees of freedom or variance, V, and the number of phases, P, the following relation is true.

$$P + V = C + 2$$

System: Water.—In the system, ice, liquid water, and water vapor, there are three phases and one component. Therefore, there can be no degrees of freedom. In other words, neither the temperature nor pressure can be changed so long as all three phases are present. If, however, one phase, as the ice, be removed, one degree of freedom is permitted and it is possible to change either the temperature or the pressure, but not both independently. If the temperature of the system is fixed arbitrarily, the pressure is therefore automatically fixed, and it is said that at any given temperature the water has a definite vapor pressure.

System: Water and Salt.—If, however, salt be added to the above system, it becomes one of two components and the sum of the number of phases and degrees of freedom is four. If the system has the three phases, solid salt, solution and vapor, there can be one degree of freedom. Let the temperature be arbitrarily fixed and the system becomes invariant, neither the pressure nor concentration of the solution being variable. It is then said that at a given temperature, salt has a definite solubility in water, and the vapor pressure of water over such a saturated solution of salt in water has a definite value. If, however, insufficient salt be added to make a saturated solution at that temperature, there would be but two phases, solution and vapor, and, therefore, it is possible to fix another variant, either the concentration of the solution or its vapor pressure. Thus it is stated that at 100° C., the vapor pressure of a solution of 1 part of Glucose in 20 parts of water is 756 mm. of mercury.

CHAPTER II

ONE-COMPONENT SYSTEMS

Vapor Pressure Curves.—The sum of the number of phases and the number of degrees of freedom in a system of one component is three. In the system, water and water vapor, it is therefore possible to fix the temperature and obtain a corresponding vapor pressure. If this be done over a wide range of temperatures, and the corresponding pressures determined, the results when shown graphically would appear as Fig. 1 which is the well-known vapor pressure curve for water.

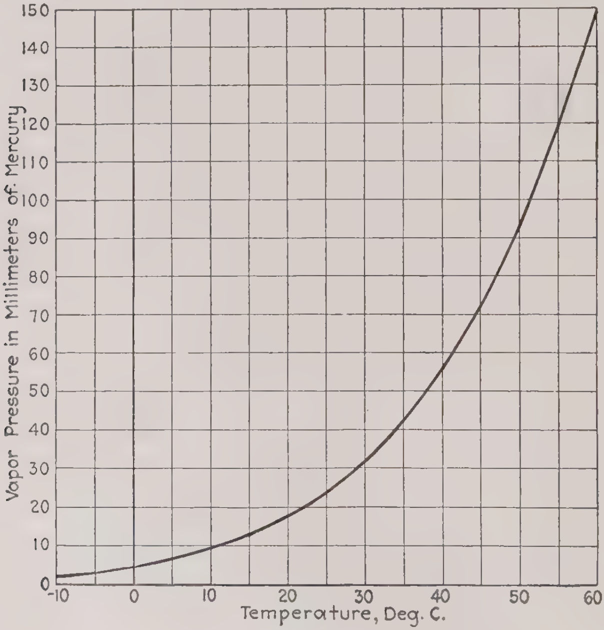

FIG. 1.—Vapor pressure curve of water.

Since, in the system, Ice-Water Vapor, there are two phases as before, it is possible by fixing the temperature, to fix the system, and, therefore, the vapor pressure and the vapor-pressure curve for Ice is obtained. This may be plotted as before.

Likewise, the system, Ice-Liquid Water, is an univariant system and fixing the pressure, for instance, will determine the temperature at which Ice will change into water or the reverse. A plot of such data will give the equilibrium curve between solid and liquid water.

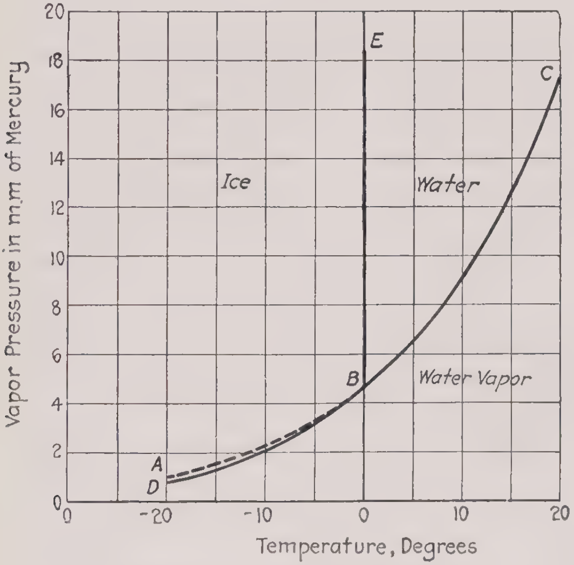

FIG. 2.—Vapor pressure diagram. System—ice, water, water vapor.

Plot these three curves as on Fig. 2, where the curve *ABC* is the vapor-pressure curve for liquid water, the curve *DB* is the vapor-pressure curve for ice, and the curve *EB* is the equilibrium curve for ice and water. At the point *B*, ice, liquid, and vapor are all in equilibrium, and, therefore, both temperature and pressure are fixed, being about 0° C. and 4.60 mm. respectively. The field *DBE* is the field of stable ice, and within that field both temperature and pressure can be varied providing there is no liquid or vapor present. The area *EBC* is the field where liquid water is stable and the pressure and temperature can both be varied if neither ice nor vapor be present. The field below the lines *DB* and *BC* is the field of superheated water vapor, which behaves like a gas, both temperature and pressure being variable.

The line *AB* is the line of equilibrium between supercooled water and vapor. The water, however, is not stable at this temperature, and if a crystal of ice be introduced, the water solidifies instantly.

Change of Temperature at Constant Pressure.—If the system, water, be raised at constant pressure, say 8 mm., from −20° C. to +20° C., the system would first consist wholly of ice. As the temperature was raised no change would occur until the system reached the temperature corresponding to the intersection of the 8–mm. line and the curve *BE*, when the ice would start to melt. The temperature would then remain constant until all of the ice was melted, when it would again rise until the line *BC* was reached. Here the liquid would start to evaporate, and the temperature would remain constant until all was in the form of steam. Further heating would then raise the temperature and the system would consist of superheated water vapor.

Unstable Conditions.—The line *AB*—that of supercooled water—lies above the vapor-pressure curve of ice—*DB*; or, the vapor pressure of the unstable liquid below 0° is greater than that of ice. It is evident from this that it is not possible for ice, liquid and vapor to exist together below 0° C., since the vapor from the water would be supersaturated with respect to the ice and would, therefore, condense upon it, eventually converting all of the liquid to solid through slow evaporation and condensation.

In general, the facts noted with respect to the system, water, apply to other systems of one component. However, since in discussing fractional distillation, systems of one component are not considered, two component systems will now be taken up.

CHAPTER III

TWO-COMPONENT SYSTEMS

Space Model of Two-component Systems.—In systems of two components, the sum of the number of phases and the degrees of freedom is four. Therefore, if but one phase be present, there are three degrees of freedom, and the composition of the phases must be considered in addition to the temperature and pressure of the system. Since any of the variables may be subject to variation, the graphical representation will involve a space model of three coordinates—temperature, pressure and concentration—as indicated in Fig. 3, where the line *OB* represents temperature, the line *OA*, pressure, and the line *OC*, concentration. Any points lying in the plane *AOB* or any plane parallel to it, will have the same composition. Any points in any plane parallel to the plane *AOC* will have the same temperature; while the plane *COB* and planes parallel to it, will be planes of constant pressure. The use, however, of space models is inconvenient, and it is usually customary to fix one condition, such as pressure, and work with a two-dimension diagram, which in this case is usually one of temperature-composition.

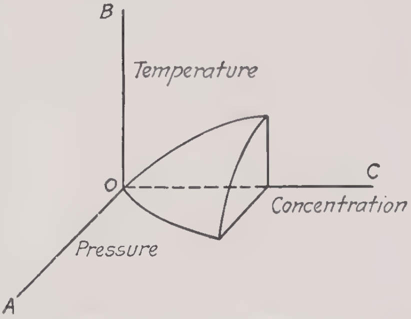

FIG. 3. -Space model—two component system.

In the study of fractional distillation, it is usual to deal with liquids and vapors, and it is unusual that solid phases are of importance. There are two common systems of liquid and vapor where there are two components; first, solution and vapor, and second, two liquids and vapor. In the first case there are two phases, and the system is bivariant. In the second case, there are three phases, and the system is univariant.

Partially Miscible Liquids.—The univariant system of two liquid phases and the vapor phase is found where two liquids are only partially soluble in each other. The relative solubility of the two components in each other may vary from almost nothing to complete miscibility. Furthermore, the degree to which one component will dissolve in the other changes with the temperature, and univariant systems frequently become bivariant on raising the temperature, due to the components becoming completely soluble in each other.

Phenol and Water.—The case of phenol and water is a good example of the latter. At 20° C., water will contain 8.40 per cent of phenol. If the temperature be raised to 50°, the solubility will be increased to 12.08 per cent.[1] Similarily, phenol will dissolve water, and at 20°, the amount present amounts to 27.76 per cent, while at 50, it has risen to 37.17 per cent. If these solubilities be plotted as on Fig. 4, it will be seen that the respective solubility curves are really one curve which passes through a maximum point at a composition of 35.90 per cent phenol, and at a temperature of approximately 68.8° C.

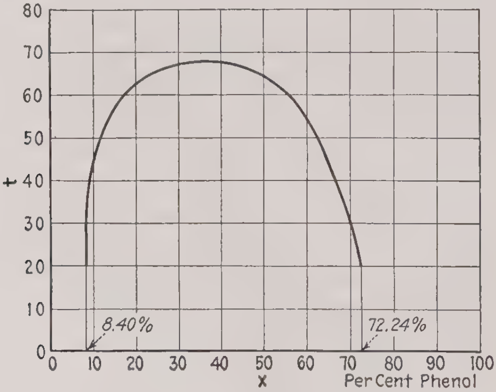

Fig. 4.—Solubility curve of phenol-water mixtures.

When phenol is added to water, and the temperature kept at 20°, it, at first, dissolves completely; but when a concentration of 8.40 per cent has been reached, the addition of any more phenol will cause the formation of a second layer, which will have

[1] (Rothmund, Z. Phys. Chem., 26, 433).

a composition of 72.24 per cent. Further addition of phenol will then have no effect upon the concentration of either liquid phase, the relative amounts of each phase changing to keep the percentages constant, until enough phenol has been added, so that the whole system contains phenol and water in the ratio 72.24 to 27.76, when any further addition of phenol will cause the disappearance of the 8.40 per cent phase, and the system will again become a system with one liquid and one vapor phase. Viewed from the standpoint of the phase rule, so long as only one liquid phase is present, it is possible to fix two conditions arbitrarily, such as, temperature and composition, but upon the appearance of the second liquid phase, the degrees of freedom are reduced to one, and, since the temperature has been fixed in the above example, the compositions of both of the two phases are therefore determined. Above the critical temperature at which both liquid phases have the same composition, the components are miscible in all proportions, and it is possible to vary either two of the temperature, composition or vapor pressure, at will.

Complete Miscibility.—It is evident that systems of two components which are partly soluble in each other at ordinary temperatures are special cases of the general one of complete miscibility, and within the limits of solubility their behavior is the same as that of the latter.

Liquid Composition.—In the chapter on "One-component Systems," it was pointed out that where the system consisted of two phases—liquid and vapor, fixing the temperature gave a definite vapor pressure, the values of which when plotted gave the vapor-pressure curve of the liquid. In the same way, in a system of two components, if the composition of the liquid be fixed, fixing the temperature will determine the vapor pressure, where there is one liquid phase and the vapor phase. If both components be volatile fixing the temperature and the composition of the liquid will also determine the composition of the vapor phase.

Temperature Composition Diagram.—By fixing the vapor pressure of a two-component system, a temperature-composition diagram can be made. Figure 5 shows a temperature-composition curve for Carbon Tetrachloride—Carbon-Bisulphide at a vapor pressure of 760 mm. Any point on the curve *ABC* gives the composition, x, of a mixture of CCl_4 and CS_2 which boils at a pressure of 760 mm. at any given temperature, t, where t is in degrees Centigrade and x is the mol per cent of CS_2. The use of the "mol per cent" or "molecular per cent" greatly facilitates calculations of vapor-pressure phenomena. By it is meant the number of molecular weights of the one component in a mixture in which the sum of the molecular weights of the respective components is 100. The dotted line *ADC* represents the composition of the vapor which is in equilibrium with the liquid at any given temperature. Thus a liquid with the composition x_1 will have a vapor pressure of 760 mm. at the temperature t_2, and the vapor in equilibrium with it will have the composition x_2.

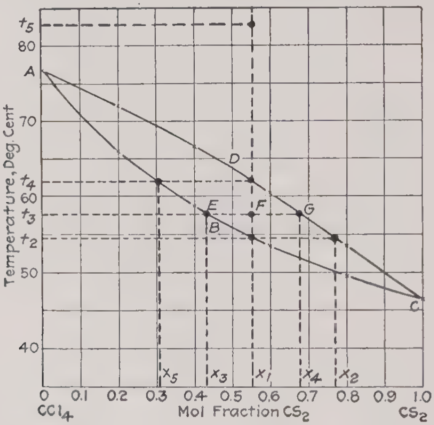

FIG. 5.—Boiling point curve for CCl_4—CS_2 mixtures.

Starting with a mixture of the composition x_1, and at the temperature t_1, there can be but one phase present, the liquid mixture of CCl_4 and CS_2. As the temperature is raised no change but the expansion of the liquid will occur until the vertical line at x_1 hits the curve *ABC*, when a vapor phase of the composition x_2 will appear. Since there are now two phases and the pressure is fixed, there can be but one variable, temperature, and the composition of the phases will depend upon it. Let the temperature then be raised to some point t_3, and the liquid and vapor compositions, being no longer independent variables must change accordingly, which they do along the curves *ABC* and *ADC* respectively, the liquid now having a composition x_3 and the vapor in equilibrium with it a composition x_4. It should be remembered that the quantity of CCl_4 and CS_2 in the system has not changed during this process, and, therefore, the change in the compositions of the liquid and the vapor include such a corresponding change in the relative proportions of each phase that the total composition of the system remains the same, x_1. Furthermore, the relative proportions of the liquid phase and vapor phase, at the temperature t_3, are as the distances *FG*, and *EF*. It will be seen that as the temperature is raised further, the proportion of liquid phase decreases, until when the temperature reaches a point corresponding to the intersection of the vertical line x_1 and the curve *ADC*, which occurs at a temperature t_4, the vapor has the same composition as the original liquid and the liquid phase disappears. At higher temperatures, there is but one, the vapor phase, and the system again becomes trivariant, so that at constant pressure it is possible to vary both the temperature and the composition of the vapor. This is the region of superheated vapor.

If the above process be reversed, the steps can be followed in the same way. Starting with superheated vapor of a composition x_1 and at a temperature t_5, condensation will first occur when the vertical line x_1 cuts the vapor line *ADC*, when liquid of a composition x_5 will separate out. Further cooling will change both the composition of the liquid and the vapor along the lines *ABC* and *ADC* respectively until the liquid has reached the composition x_1 when all the vapor will have disappeared.

Equilibrium in Fractional Distillation.—It will be noted that in both the above heating and cooling processes, the liquid phase and vapor phase have been kept in equilibrium. Also, it will be noted that there can be liquid and vapor in equilibrium with each other only between the temperatures t_2 and t_4, and the composition of the liquid phase can vary only between the limits x_1 and x_5. It is therefore evident that if the two components, CS_2 and CCl_4, are to be separated into the pure substances by fractional distillation, either the system must be placed in unstable equilibrium, or the system itself must be changed.

General Methods of Fractionation.—There are two general methods by which fractionation can be obtained, successive distillation of the condensed distillates, and fractional condensation, both methods depending on the separation of the liquid from the vapor while the phases are in equilibrium.

Successive Distillation.—The first method, successive distillation of the condensed distillates, can be best shown by referring to Fig. 5. Starting with a large amount of liquid of the composition x_5 which boils at 760 mm. pressure at a temperature t_4, a small amount of vapor, of the composition x_1 is removed from the apparatus and condensed, giving a liquid of the composition x_1. Let this new liquid again be distilled, and the first portion of the distillate will have the composition x_2. Continuing this process, the successive compositions of the distillate can be estimated by following the series of dotted steps, which eventually approach the point C, pure CS_2, as a limit.

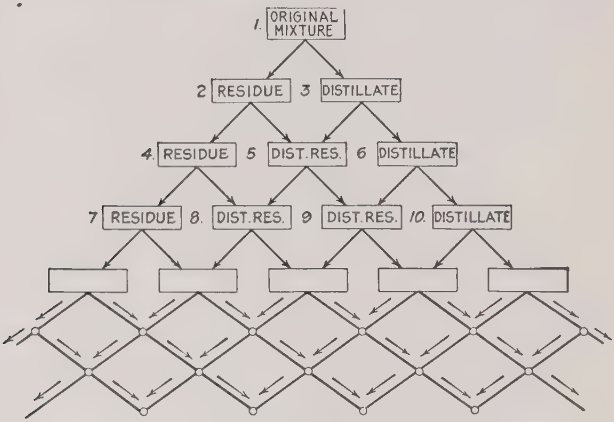

FIG. 6.—Fractionation diagram.

The removal of any vapor of a composition x_1 from the liquid of the composition x_5 will change the composition of the liquid in the direction of pure CCl_4. Therefore, if the distillation of the liquid be continued, the composition will approach pure CCl_4 as a limit, and the last of the liquid to be distilled would have this composition.

It is therefore possible by a systematic series of distillations to separate any mixture of CS_2 and CCl_4 into practically pure CS_2 and pure CCl_4. This systematic fraction may be shown diagrammatically as in Fig. 6, in which the original mixture (1) is divided into a distillate (3) and a residue (2). (3) and (2) are then distilled separately and produce distillates and residues, the distillate from (2) and the residue from (3) being combined into a new liquid (5) which is again distilled with (4) and (6) to continue the separation. This process is continued until practically complete separation is obtained. Such a process is sometimes carried out in the laboratory, but it is extremely tedious, and the same result can be obtained in other, much more convenient ways.

Multiple Distillation.—Suppose an apparatus as in Fig. 7, consisting of a series of distilling kettles, *A*, *B*, *C*, etc., each kettle containing a heating coil, and necessary connections for vapors and liquids. Suppose that kettle *A* contains a liquid mixture of CS_2 and CCl_4, of the composition x_5 as on Fig. 5, the kettle *B*, a liquid of the composition x_1; the kettle *C*, the composition x_2, and so on. The liquid in *A* boils at t_4, that in *B* at t_2, and that in *C* at t_6. Since the vapor leaving *A* is at a temperature t_4, which is higher than the boiling temperature in *B*, t_2, then, if the vapor

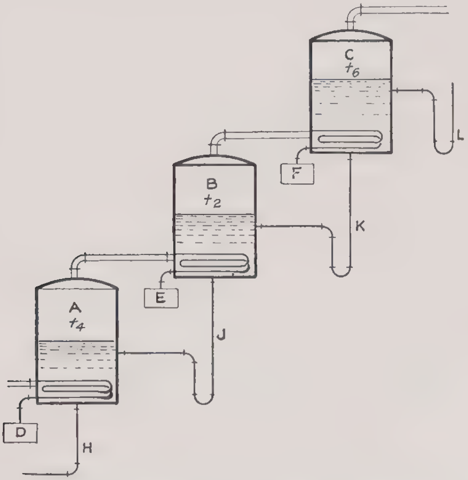

FIG. 7.—Diagram of multiple distillation.

from *A* be led into the heating coils of *B*, it will give up its heat to the contents of *B*, boiling the liquid, and itself being condensed. The vapor from *B*, if led into the heating coils of *C*, will in the same way, boil the liquid in *C*, the vapor being itself condensed as before. The condensed vapors in the coils may be drawn off into receivers *D*, *E*, *F*, etc. However, since the composition of the liquid in *B* was selected to be the same as that of the vapor coming from the kettle *A*, from Fig. 5, the condensed vapor in the coils of *B* can be allowed to mix with the contents of *B* instead of being withdrawn into the receiver *E*. Now, since the vapor from *A* is being mixed with the liquid in *B*, and since there is a heat interchange between the two, it is much simpler to blow the vapor directly into the liquid, thus dispensing with the coils.

As the liquid in the kettle *B* distils, giving off a vapor richer in CS_2 than itself, the concentration of the liquid tends to become poorer in CS_2, in spite of the addition to it of the vapor from *A*. Therefore, if it be withdrawn continually through the pipe *J* and run into the kettle *A*, the tendency for the liquid to become poorer in CS_2 will be reduced, and the contents of the kettle *A* will, at the same time be enriched. In the same way, the liquid in *C* is allowed to flow continuously back into the kettle *B*.

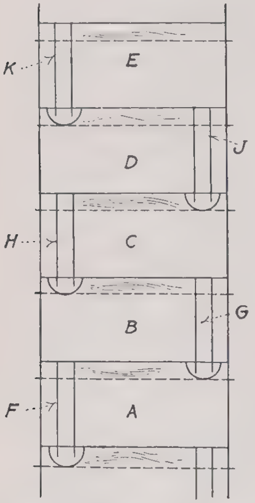

Fig. 8.—Diagram of fractionating column.

Continuous Fractional Distillation.—By this process, therefore, if a constant supply of vapor be furnished to the kettle *A*, a continuous fractional distillation can be obtained. Furthermore, since each kettle represents a change in composition corresponding to one step of the dotted lined steps in the diagram on Fig. 5, if there are as many kettles as there are required steps to pass from practically pure CCl_4 to practically pure CS_2, such an apparatus will separate the mixture into the practically pure components, continuously, and with but little labor.

Fractionating Column.—The above device is the basis upon which the fractionating (or dephlegmating) column of a fractionating still is made. A portion of a simple column is shown on Fig. 8. This column contains perforated plates, dividing it into the sections *A*, *B*, *C*, etc. Each of these sections has the same function as a kettle in the previous apparatus. The vapor from the liquid on the plate *A*, passes through the small holes in the plate *B* and coming into contact with the colder liquid on the plate *B*, is condensed, thereby giving up its heat to the liquid on the plate, and causing it to boil. The excess liquid on the plate *B* overflows onto the plate below through the pipe *F*.

Entrainment.—The analogy between this fractionating column and the series of kettles would be complete if the vapor leaving the liquid on the plate had the equilibrium composition as predicted from curves as on Fig. 5. But, unfortunately, no design has been able to wholly prevent some of the vapor from the plate below passing through the liquid on the plate, without coming into equilibrium with it. The vapor above any plate, therefore, is a mixture of the vapor from the liquid on that plate, and of the vapor from the plate below, and, therefore, it will contain less of the volatile component than would be the case if complete equilibrium were reached. The ratio of the actual composition of the vapor over the plate, when the *reflux ratio*, which will be explained in Part II, is infinite, to the equilibrium composition of the vapor, is a measure of the efficiency of the plate as a fractionating device.

The numerous modifications of the fractionating column will be discussed in the chapter devoted to that subject.

Fractional Condensation.—The second general method by which fractionating can be obtained, is fractional condensation. Referring again to Fig. 5, suppose a mixture of CS_2 and CCl_4 vapor with the composition x_1 and at the temperature t_5. It was stated that upon cooling, condensation would begin when the x_1 vertical line reached the vapor line *ADC*, and that the liquid which appeared would have the composition x_5. If, now, the liquid be removed from contact with the vapor as rapidly as it appears, and since the liquid is poorer in the more volatile component, CS_2, than the vapor, the vapor will grow progressively richer in CS_2 as the temperature drops until, as the last of the vapor condenses, its composition will have reached that of pure CS_2. It is, therefore, possible to separate the pure more volatile component from a mixture by vaporizing the mixture, and then condensing the vapor gradually, withdrawing the condensate as rapidly as it appears. But it is obvious that such a process would be most inefficient since all of the liquid must be vaporized and condensed in order to obtain the last portion of remaining vapor as practically pure component. Actually, fractional condensation is combined with successive vaporization, and with a modification of successive vaporization known as washing or scrubbing which will be discussed below, to produce efficient fractionation.

Classes of Binary Mixtures.—Binary mixtures of volatile liquids, miscible in all proportions, are divided into three main classes. These three classes are illustrated by Fig. 9, where

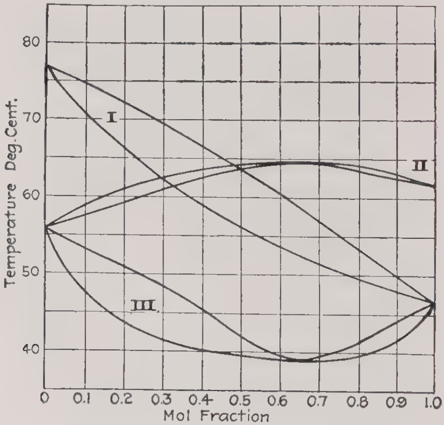

Fig. 9.—Types of binary mixtures.

Curve I is the liquid-vapor curve for Carbon Tetrachloride—Carbon Bisulphide mixtures at 760 mm. which was shown on Fig. 5. This type of mixture can be separated into its components by fractional distillation.

Maximum Boiling Point.—Curve marked II is the boiling-point curve for mixtures of Acetone and Chloroform. This curve passes through a maximum point at approximately a composition of 65 mol per cent Chloroform, at a temperature

64.6°C., which is higher than the boiling temperature of either pure component, and the liquid and vapor curves are tangent to each other at this maximum point. Evidently, a liquid of a composition corresponding to this maximum, when raised to its boiling point, would produce a vapor of the same composition as the liquid, and, therefore, the two components cannot be separated by fractional distillation.

If a vertical line be drawn through this maximum boiling point, the diagram will be divided into two parts, and the section of the curve in each part will resemble the simple type of Curve I. It can, therefore, be stated that in such a system of two components, where there exists a maximum boiling point, any mixture of these components can be separated by fractional distillation into one pure component and the mixture of constant boiling point, but that it is impossible, by fractional distillation, to separate such a mixture into both of its components. Furthermore, in a fractional distillation of such a mixture, the distillate will be richer in the pure component since it boils at the lower temperature, and the residue will be richer in the constant boiling mixture.

Minimum Boiling Point.—Mixtures represented by Curve III are the type having minimum boiling points. Such mixtures behave exactly like those of maximum boiling points, except that upon distillation the distillate is richer in the constant-boiling mixture, while the residue is richer in the pure component. The best known case of such a mixture is that of ethyl alcohol and water, which will be discussed later in detail.

Since in such systems there are two phases, liquid and vapor, and if the condition is fixed that both phases have the same composition as is the case with the mixtures of constant boiling point, then there can be but one other degree of freedom, and if the pressure be fixed, then the system is invariant and it is impossible to change the composition of the constant-boiling-point mixture. But changing the pressure will allow a corresponding change in the composition of the mixture. Also the addition of another component, such as a salt, to the liquid, will allow a change in the composition. This latter method is in common use, industrially, for this purpose, and will be discussed later.

CHAPTER IV

MORE COMPLEX SYSTEMS

Two-component systems have thus far been the subject of consideration, but fractional distillation is by no means confined exclusively to such systems, since most industrial mixtures contain greater or less amounts of impurities, and fractional distillation is often depended upon to separate the products from them. It is frequently true, however, that the mixtures to be separated consist largely of two components and that the other components are present in relatively small amounts. If this is the case, it is customary to consider the system preliminarily as a two-component system and then modify the design to allow for the other components. In many cases, however, this cannot be done, and the system must be considered from the start as a multi-component system.

Three-component Systems.—In systems of three components, the sum of the number of phases and the degrees of freedom is five. In order for such a system to be invariant, there must be five phases present. In systems consisting of liquids and vapors, however, it is rare that there are present more than two liquid phases and one vapor phase and such a system, therefore, has two degrees of freedom. For instance, ethyl ether and water are partially soluble in each other and when mixed in proportions greater than the limits of solubility, form two liquid phases, one a solution of water in ether, and the other a solution of ether in water. Such a system of two components, with two liquid phases and one vapor phase, has one degree of freedom, and, therefore, if the temperature be chosen, the system becomes fixed, and the compositions of the liquids, of the vapor, and the vapor pressure of the system are fixed. If, however, some ethyl alcohol be added to the system, it now becomes one of three components, and it is possible to fix some other condition in addition to the temperature; for instance, the vapor pressure. Or, in other words, the temperature at which such a mixture will boil at atmospheric pressure, that is, the temperature at which the vapor pressure becomes equal to the barometric pressure, may also be varied. If the temperature and pressure are fixed, of course, the compositions of the liquid and vapor phases become fixed.

System: Ether, Alcohol, Water.—In the system, ether, water, alcohol, if alcohol be added to the ether and water, the solubility of ether in the water is increased, and the solubility of the water in the ether is increased. If sufficient alcohol be added, a point is reached when the ether phase and the water phase contain the same amounts of ether, alcohol and water, and any further increase in the amount of alcohol, will produce a system of one

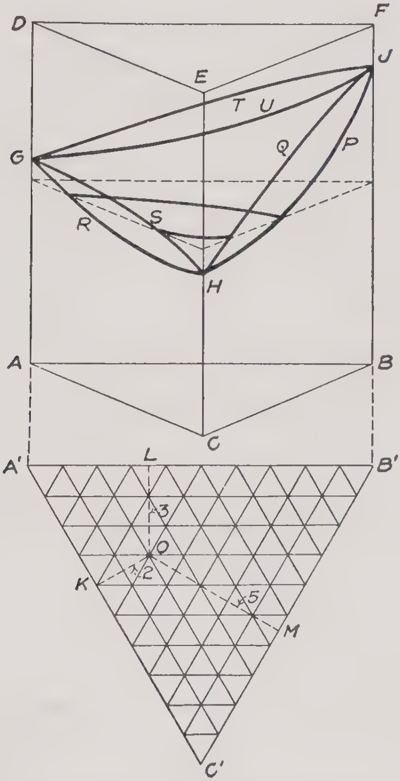

Fig. 10.—Diagram of three component system.

liquid phase, where ether, water and alcohol are completely soluble in each other. Under this condition, there are three degrees of freedom, and the temperature, pressure, and composition of the liquid, for example can be fixed. This will fix the composition of the vapor phase in equilibrium with the liquid phase. It is difficult to show diagrammatically, three-component systems. One method of graphical representation is shown on Fig. 10 which consists of a prism erected on an equilateral triangle *ABC*. The sides of the triangle are divided into 10 or 100 equal divisions, representing mol fractions of the components. Thus the line *CB* represents mixtures of the pure components C and B and any point on the line indicates their mol fractions. Also, any point on the line *AC* represents mixtures of the components A and C, and any point on the line *AB*, mixtures of the components, A and B.

It is a property of such a triangle that if the length of the perpendicular from any apex to the opposite side be unity, the sum of the perpendiculars from any point within the triangle to the three sides, will also equal unity. Therefore, since the sides are divided uniformly as mol fractions, the length of the perpendiculars from any point within the triangle to the respective sides will indicate the mol fraction of the component, whose apex lies opposite the side of the triangle to which the perpendicular is drawn. Thus, the point *O* has the perpendicular line *OK* drawn to the line *AC*, having a length equal to 0.2. Therefore, the mol fraction of the component B is 0.2. In the same way, the mol fraction of C is 0.3 and the mol fraction of A is 0.5, totaling 1.0. Any mixture of A, B and C may, therefore, be indicated by properly locating its composition on this triangle.

If the vertical dimension of the prism represents temperature, on such a space model, it is possible to illustrate changes in temperature and composition, but not changes in pressure. Just as in two-component system, the temperature-composition diagram was at constant pressure, so in this case the whole space model is at constant pressure. The pure component B boils at atmospheric pressure at a temperature corresponding to the point *J*. Pure C boils at a temperature corresponding to H, while pure A boils at the temperature G. The plane surface *CEFB* of the prism, then, is exactly the same as the temperature-composition diagram used for two-component systems, and the boiling-point curve for mixtures of C and B can be drawn as before, together with the vapor curve in equilibrium with it, as shown by the curves *HPJ* and *HQJ* respectively. In the same way the boiling point and vapor curves for mixtures of A and C can be drawn in the plane *ADEC*, and the boiling point and vapor curves of mixtures of A and B can be drawn in the plane *ADFB*. It will be seen that the three boiling point curves *HPJ*, *GRH*, and *GVJ*, from the boundaries of a surface. This surface represents the boiling temperatures of mixtures of A, B and C, whose compositions are determined as above. In the same way, the vapor lines, *HQJ*, *GSH*, and *GTJ*, form another surface which represents the vapor in equilibrium with the liquid mixture. A horizontal plane represents a plane of constant temperature, and such a plane, cutting both liquid and vapor surfaces, will form lines which indicate compositions of the vapor phase which are in equilibrium with the liquid mixtures which boil at that temperature. Such an intersection of a constant temperature plane with the liquid and vapor surfaces is shown on Fig. 11 where the line *abc* is the intercept with the liquid surface, and the line *def* that with the vapor surface. Since there are two phases, liquid and vapor, and the pressure and temperature have been fixed, there is one degree of freedom. If, now, the composition of the liquid with respect to one component is fixed, say 10 mol per cent of A, the line representing a mol fraction of A of 0.10, *gh*, will cut the liquid line *abc* at some point *x*. A liquid of this

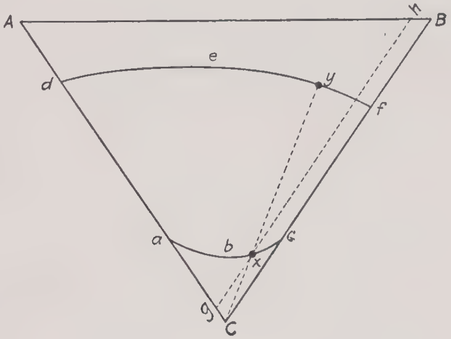

Fig. 11.—Constant temperature diagram. Three component space model.

composition will boil at the fixed temperature and pressure. The vapor in equilibrium with the liquid x will have some fixed composition y which may or may not be on the projection of the line connecting C and x.

Ternary Constant-boiling Mixtures.—The system illustrated on Fig. 10 is one in which there are no constant-boiling mixtures, and separation by fractional distillation can be complete. Very commonly, however, one pair of the three will have a constant-boiling mixture, and often two pairs of the three will have such mixtures. When this latter occurs, constant-boiling mixtures of the three components will be obtained. This is very common in cases where one of the components is only partly soluble in the others; for example, the mixture of benzene, ethyl alcohol and water. This system has a constant-boiling mixture, boiling at a temperature considerably below any of the pure components, and containing more water than the constant-boiling mixture of alcohol and water. This system is one used in the manufacture of absolute alcohol.

Partially Miscible Components.—Occasionally, the presence of a partly soluble component, and a binary constant-boiling mixture, fails to produce a ternary C.B.M. For instance, iso-amyl alcohol is only partly soluble in water, and ethyl alcohol forms a C.B.M. with water; but no ternary C.B.M. is formed, since the alcohol-water C.B.M. has a lower boiling temperature than the iso-amyl alcohol-water mixture in the presence of alcohol. This permits the separation of the iso-amyl alcohol from the ethyl alcohol and water, as illustrated in the recovery of fusel oil in the rectification of fermentation alcohol.

CHAPTER V

THE GAS LAWS

The principles involved in fractional distillation are fundamentally the elementary laws of physics and thermodynamics. Many of the so-called physical laws are, however, very limited in their applications, and do not apply exactly throughout the whole range of conditions included under distillation. Often, the laws hold exactly only for the non-existent perfect gases, and for perfect solutions, and hold only approximately for actual gases and solutions which are said to approach perfect gases and solutions to a greater or lesser degree according to their behavior in relation to the perfect gas and solution laws. However, in engineering work, the large number of more or less indeterminate factors which come into every problem, render exact solutions very difficult, and approximate solutions are usually sufficient. Under these circumstances, the perfect gas and solution laws often give results which are sufficiently close for engineering purposes. It is usually possible to devise wholly empirical equations which describe the behavior of actual gases and solutions exactly within the limits of the data, and these empirical equations are frequently of very great use in distillation calculations. But such equations have the disadvantage that they bear no theoretical relation to other equations and are incapable of safe extrapolation. It is, therefore, very much safer to use the perfect gas and solution laws wherever they can be used and make use of empirical equations as little as possible.

Boyle's Law.—The first of the theoretical laws which is of importance in distillation, is the Law of Boyle, which states that at constant temperature the volume of a given gas is inversely proportionate to its pressure, or

$$PV = \text{constant}$$

Thus, doubling the pressure on a given amount of a gas at constant temperature should halve its volume.

Gay-Lussac's Law.—If, however, the temperature of a given amount of a gas be raised, either the gas will expand or its pressure will increase, and it has been found that at 0°C., raising the temperature 1°C. will cause a gas to increase in volume $\frac{1}{273}$ of its volume, at constant pressure; or inversely, the pressure will be increased $\frac{1}{273}$ of its pressure at 0°C., if heated at constant volume. This temperature effect is known as the Law of Gay-Lussac.

Absolute Zero.—Since the volume of a gas diminishes $\frac{1}{273}$ of its volume at 0°C. for each degree it is cooled, when the gas has been cooled to −273°C., or −273.1°C. exactly, its volume should be zero. −273°C. is, therefore, known as the Absolute zero. In English units this corresponds to −459.6°F. This would occur only with a perfect gas, however, and it has been found that actual gases condense to the liquid state before −273°C. is reached.

Perfect Gas Equation.—The laws of Boyle and Gay-Lussac can be combined to give the equation

$$PV = NRT$$

where P is the pressure exerted by the gas, V is its volume, N is the number of molecular weights or mols of the gas present, T is the temperature at which the gas exists, when measured from absolute zero, and R is some constant, known as the Gas Constant, whose value varies according to the units which are selected for P, V and T. Thus, when T is in degrees Centigrade absolute, P is in atmospheres pressure and V is in liters, R will have the value of 0.08207 (0.082).

Molal Volume.—The volume which one molecular weight in grams of a gas will occupy at 0°C. and 1 atmosphere pressure may be found as follows:

$$1 \times V = 1 \times 0.08207 \times 273.1$$
$$V = 22.41 \text{ liters.}$$

The value −22.4 liters—of 1 gram mol of a gas at 0°C. and 1 atmosphere pressure, is a very convenient figure to remember and frequent use will be made of it. In the same way, the value of the mol in English units may be determined and has been found to be 359.0 for 1 lb. mol of a gas at standard conditions (32°F. and 29.92 in. of mercury).

As has been stated above, no gases follow the laws of the PV = NRT equation exactly. The greater the distance of a gas from its saturation temperature, and the lower the pressure, the more nearly will the gas behave like a perfect gas. For the so-called permanent gases such as Oxygen, Hydrogen, Nitrogen, and so on, the PV = NRT equation holds almost exactly for ordinary temperatures and pressures. But even these show marked deviations as the pressures increase and the temperatures approach the liquifying point. Consequently, other equations have been worked out to describe the behavior of these gases more exactly, the most notable being that of Van der Waal's

$$\left(P + \frac{a}{V_2}\right)(V - b) = RT$$

which is the PV = NRT equation with N = 1, and P and V corrected for the internal-pressure effect of the molecules of a gas and for the actual volumes of the molecules of the gas themselves. This equation holds very well for most gases up to extremely high pressures, and in some cases for the liquefied gases also, but it is a difficult equation to handle and is used very little in engineering work.

Precision of Perfect Gas Laws.—In order to show the applicability of the equation PV = NRT, the following table has been calculated for 1 lb. of steam. Thus it is evident that for saturated vapors, the above equation is good to about 2 per cent., while for superheated vapors, it becomes increasingly more accurate as the degree of superheat increases. Since, in most distillation work, errors of 2 per cent. in the volume of vapors are not serious, the use of this equation may be permitted.

Temperature, degrees Fahrenheit	Pressure, pounds per square inch	Specific volume, cubic feet		Difference	Condition of vapor
		Actual	Calculated		
212	14.70	26.81	27.21	0.40	Saturated
250	15.00	27.84	28.18	0.34	Superheated
400	15.00	33.96	34.13	0.17	Superheated
600	15.00	41.98	42.09	0.11	Superheated

Dalton's Law.—When gases are mixed together, it has been found that each gas exerts a pressure exactly the same as if that same amount of gas were present in the same space alone, and that the total pressure exerted by the mixture of the gases is exactly equal to the sum of the individual pressures of each of the gases if each were present alone in the same space. The pressure of the individual gas is called its partial pressure, and the above law is known as Dalton's Law of Partial Pressures.

Since the equation $PV = NRT$ is substantially true for all gases and vapors, the volume of one mol of all gases must be the same at the same temperature and pressure. It is therefore evident from Dalton's Law that the partial pressure of a gas in a mixture of gases must be proportional to the ratio of the number of mols of the gas present to the total number of mols of all the gases present. This ratio is called the mol-fraction (x) and the rule may be stated

$$p = Px$$

where p is the partial pressure of the gas in the mixture of gases containing x mols of the gas per mol of the mixture, and where P is the total pressure of the mixture. It also follows that the per cent by volume of a gas in a mixture is equal to 100^x.

Composition of Air.—Thus, air contains 20.9 per cent Oxygen, 78.1 per cent Nitrogen and 1.0 per cent Argon, by volume. Therefore, when air exists at 760 mm. pressure, the partial pressure of the Oxygen will be

$$\frac{20.9}{100} \times 760 = 159 \text{ mm.}$$

It is often necessary to convert per cent by volume of a gas to per cent by weight, or the reverse. The method is indicated by the following example.

Calculation of Weight Per Cent.—Calculate the weight composition of the Oxygen, Nitrogen, and Argon in air.

The molecular weight of Oxygen is 32.00
The molecular weight of Nitrogen is 28.02
The molecular weight of Argon is 39.88

If 100 mols of air are used, the weight of the

Oxygen will be $20.9 \times 32.00 = 668.8$
Nitrogen will be $78.1 \times 28.02 = 2,189.0$
Argon will be $1.0 \times 39.88 = 39.88$
Sum 2,898.00

$$\text{Weight per cent Oxygen} = \frac{668.8}{2{,}898} \times 100 = 23.1 \text{ per cent}$$

$$\text{Nitrogen } \frac{2{,}189}{2{,}898} \times 100 = 75.5 \text{ per cent}$$

$$\text{Argon} = \frac{39.88}{2{,}898} \times 100 = 1.38 \text{ per cent}$$

Calculation of Mol Per Cent.—The reverse calculation, the conversion of weight per cent to mol or volume per cent is shown as follows:

What is the mol per cent of the Acetone and Ethyl Alcohol in a vapor containing equal parts by weight of each?

Molecular weight of Alcohol (C_2H_5OH) = 46.06
Molecular weight of Acetone ($(CH_3)_2CO$) = 58.07

if 100 parts of the mixture are used the mols of each vapor will be

$$\frac{50}{46.06} = 1.110 \text{ mols Alcohol}$$

$$\frac{50}{58.07} = \underline{0.860} \text{ mols Acetone}$$

$$\text{Sum } 1.970$$

$$\text{Mol per cent Alcohol} = \frac{1.110}{1.970} \times 100 = 56.3 \text{ per cent}$$

$$\text{Mol per cent Acetone} = \frac{0.860}{1.970} \times 100 = 43.7 \text{ per cent}$$

CHAPTER VI

SOLUTIONS

Clapeyron Equation.—It was shown that where a pure liquid is in contact with its vapor, the vapor pressure of a liquid is fixed at any given temperature. The change of the vapor pressure with the temperature is shown exactly by the Clapeyron equation, which may be developed thermodynamically.

$$\frac{dp}{dT} = \frac{L}{(V - Vo)T}$$

where $\frac{dp}{dT}$ is the change in pressure with the temperature, L is the latent heat of vaporization of one mol of the liquid, V is the volume of one mol of the vapor, Vo the volume of one mol of the liquid, and T the absolute temperature at which vaporization takes place.

The heat of vaporization changes with the temperature, but not rapidly, and for small temperature ranges, it is possible to consider L a constant. Also, PV = NRT may be considered to hold for small temperature ranges, and Vo is usually very small compared with V, so that V − Vo practically equals V.

Approximate Clapeyron Equation.—Making use of these approximations the Clapeyron equation may be written

$$\frac{dp}{dt} = \frac{L}{\frac{RT^2}{p}}$$

which when integrated between limits gives

$$\ln \frac{p_2}{p_1} = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where *ln* represents Napierian logarithms or $\log_e$, and $\log_e = \log_{10} \times 2.303$.

Benzene.—An example of the use of this equation is given for Benzene (C_6H_6), which boils at 80.36°C. under 760 mm. pressure and whose latent heat of vaporization is 7,250 calories per gram mol. When L is measured in calories, R must be used in corresponding units and it has the value 1.9885 (1.99)

$$\ln \frac{p_2}{760} = \frac{7{,}250}{1.99}\left(\frac{1}{273.1 + 80.36} - \frac{1}{T_2}\right)$$

Pressure in millimeters	Temperature degrees Centigrade		Difference, degrees
	Observed	Calculated	
181	40.0	37.5	−2.5
389	60.0	59.0	−1.0
760	80.36		
1,748	110.0	111.1	+1.1
3,520	140.0	142.3	+2.3

A table giving values of the latent heat of vaporization of the more common volatile liquids will be found in the Appendix (Table V).

It is possible to obtain a close approximation of the true vapor pressure curve of a liquid by expressing L as a function of the temperature

$$L = a + bT + cT^2 + \text{etc.}$$

The approximate Clapeyron equation then becomes

$$\frac{\frac{dp}{p}}{dt} = \frac{a + bT + cT^2 + \text{etc.}}{RT^2}$$

$$\frac{\frac{dp}{p}}{dt} = \frac{a}{RT^2} + \frac{b}{RT} + \frac{c}{R}$$

which when integrated has the form

$$\ln p = -\frac{a}{RT} + \frac{b}{R}\ln T + \frac{c}{R}T + \text{constant.}$$

Empirical Vapor-pressure Equations.—However, since the relation of L and T has been accurately studied for but few liquids, and since the exact vapor pressure curves are available for almost all of them, this last equation has very limited application. It is commonly in use for steam; for instance, the Marks equation:

$$\log_{10} p = 10.515354 - \frac{4{,}873.71}{T} - 0.00405096T + 0.000001392964\,T^2$$

where p and T are expressed in pounds per square inch and degrees Fahrenheit absolute respectively. It must be realized that this type of equation is wholly an empirical one, since it is based on an empirical relation between L and T.

Raoult's Law.—The introduction of a dissolved substance or solute into a volatile liquid lowers the vapor pressure of the liquid if the solute is non-volatile, or lowers the partial vapor pressure of the solvent, if the solute is volatile. It has been found that the vapor pressure lowering is proportional to the mol fraction of the dissolved substance, and the relation may be expressed by the equation

$$p = p_0 x_0$$

where p is the partial vapor pressure of the solvent, p_0 is the vapor pressure of the pure solvent, and x_o is the mol fraction of the solvent in the mixture. This is known as Raoult's Law of Vapor Pressure Lowering. It can be predicted qualitatively from the Phase Rule, since the addition of another substance to a pure liquid makes a two-component system, and it is, therefore, necessary to fix the composition of the liquid (or the vapor) as well as the temperature, in order to fix the vapor pressure.

Vapor Pressure of Sugar Solution.—For example, it has been possible to calculate the vapor pressure of a 10 per cent. cane sugar solution in water at 100°C.

Thus,

Molecular weight of water = 18
Molecular weight of sugar = 342

$$\frac{0.10}{342} = 0.000292$$

$$\frac{0.99}{18} = 0.055$$

$$\text{Sum} \quad 0.055292$$

$$\text{Mol fraction of the sugar} = \frac{0.000292}{0.055292} = 0.00528$$

$$\text{Mol fraction of the water} = 1. - 0.00528 = 0.99472$$

The vapor pressure of pure water at 100°C. = 760 mm.

Therefore vapor pressure of the 10 per cent sugar solution would be 0.99472 × 760 = 756 mm. This example for the case of a non-volatile material dissolved in a volatile solvent is similar to the case of a volatile material dissolved in a volatile solvent, the only difference being that the partial pressure of the solvent and not the total vapor pressure of the mixture must be taken into consideration. For instance, in order to calculate the partial pressure of benzene over a mixture containing 5 per cent. by weight of toluene in the benzene at 80°C., a similar method is used. Thus, the molecular weight of benzene is 78.1. The molecular weight of toluene is 92.1. In 100 parts by weight of the mixture there will be $\frac{5}{92.1} = 0.0543$ mols of toluene and $\frac{95}{78.1} = 1.216$ mols of benzene. The total number of mols present in 100 parts of the mixture is 1.270.

The mol fraction of the toluene $= \frac{0.0543}{1.270} = 0.0427$

The mol fraction of the benzene $= 1.0 - 0.0427 = 0.9573$.

The vapor pressure of pure benzene at 80°C. is 753.6 mm.

Therefore, the partial pressure of benzene over this mixture will be $753.6 \times 0.9573 = 721.5$ mm.

Limits of Raoult's Law.—The use of Raoult's law for the purpose of calculating the partial pressure of the solvent in any solution is limited in application to dilute solutions, usually of less than 5 per cent. dissolved solute. In some cases, however, as for instance the case of mixtures of benzene and toluene, Raoult's Law applies to considerably higher concentrations, while in other cases, such as mixtures of alcohol and water, Raoult's Law practically does not hold at all. Furthermore, if the dissolved material is an electrolyte, such as an acid, an alkali or a salt, which is ionized in solution, the vapor pressure lowering is increased, depending upon the degree of ionization of the dissolved material. For instance, a solution of acetic acid and water will conduct electricity, indicating that the acetic acid is ionized to a certain extent. Experiments have shown that dilute acetic acid of a strength approximately $\frac{1}{10}$ of a molecular weight per 1,000 grams of water, that is, 6 grams of acetic acid in 1,000 grams of water, is ionized approximately 1.34 per cent at 25°C. The vapor pressure lowering of the water in a solution of this concentration, therefore, will be increased by 1.34 per cent over the lowering which would be calculated from the molal concentration of the acetic acid if it were not ionized. Thus, the equivalent number of mols of acetic acid present in this solution would be 1.0134 × $\frac{1}{10}$ mols in 55.5 mols of water. Since the vapor pressure of pure water at 25°C. is 23.55 mm., the vapor pressure lowering would be

$$\frac{23.55 \times 0.10134}{55.5 + 0.10134} = 0.429 \text{ mm.}$$

The partial pressure of the water vapor, therefore, over this solution would be $23.55 - 0.429 = 23.12$ mm.

Henry's Law.—There is another rule for solutions known as Henry's Law which states that the partial pressure over the mixture of a volatile solute dissolved in a solvent, is proportional to the mol fraction of the solute in the mixture, or

$$p = ax$$

where p is the partial pressure of the dissolved substance, x is the mol fraction of the dissolved substance in the mixture and a is some constant. It is obvious that if the constant a has the same value as the vapor pressure of the pure solute at the same temperature, the equation is the expression for Raoult's Law which is, therefore a limiting case of Henry's Law. It is not common, however, for a mixture of two volatile materials to follow Raoult's Law throughout the entire range of compositions. Therefore, the constant a is usually different from p_0, the vapor pressure of the pure material. In the case of benzene and toluene, for instance, a is practically equal to p_0 and the partial pressure of the dissolved substance present in the smaller proportion can be calculated from Raoult's Law with considerable precision. Thus, in the case cited above, 5 per cent by weight solution of toluene in benzene, it was noted that the mol fraction of toluene was 0.0427. Therefore, if the vapor pressure of pure toluene at this temperature be multiplied by this figure, the partial pressure of toluene in the vapor above this mixture will be obtained. The vapor pressure of pure toluene at 80° is 291 mm., giving a partial pressure of the toluene of 12.4 mm. The total vapor pressure of the liquid, which is the sum of the partial pressures of the two components, will be the sum of the partial pressures of the benzene and toluene, or 735.9 mm.

Partial Pressure of Ammonia over Water.—In most cases, however, the constant a is not equal to p_0 and it is necessary to determine experimentally the value of a at any given temperature. This has been done for a large number of mixtures. For instance, the partial pressure of ammonia, NH_3, above an aqueous solution of ammonia containing one molecular weight, 17 grams, per 1,000 grams of water at 25°, is 13.47 mm.

In the expression, $p = ax$, $p = 13.47$ mm.

$$x = \frac{1}{\frac{1000}{18}} = 0.018$$

The value of the constant, a, therefore, is $\frac{13.47}{0.018} = 748.$

Using this value of a it would be possible to calculate by Henry's Law the partial pressure of ammonia over a 0.5 molal solution at the same temperature.

$$p_0 = 748 \times \frac{0.5}{\frac{1000}{18}} = 6.74$$

The experimentally determined value for this strength is 6.65. In the same way, the partial pressure of ammonia over a 0.25 molal solution would be 3.37 mm. while the experimentally determined figure is 3.32 mm.

Chemical Combinations.—The above figures indicate the reliability of Henry's Law and its application to very dilute ammonia solutions. It should be noted, however, that ammonia combines with water to form ammonium hydroxide according to the reaction $NH_3 + H_2O = NH_4OH$. It would be expected from this equation that the more dilute the solution of ammonia, the greater the proportion of ammonia in the solution will be present in the form of NH_4OH rather than NH_3. In other words, where a volatile material combines chemically with the solvent, the vapor pressure of the volatile material will be less than that calculated from Henry's Law and the divergence will be greater the more dilute the solution. For such mixtures, it is, therefore, safe to use Henry's Law only over small dilution ranges.

Limits of Henry's Law.—Where the volatile materials do not combine chemically, as in the case of mixtures of benzene and toluene, Henry's Law will be found to apply nearly exactly over a fairly wide range of concentrations. In general, however, its range of accuracy has an upper limit of somewhere between 5 per cent and 10 per cent of the dissolved substance.

Empirical Equations.—It will be seen, therefore, that Raoult's Law and Henry's Law apply for either very small or very great concentrations of the volatile material. For intermediate concentrations, however, there are no physical laws which are applicable and recourse must be had to experimentally determined data. It is possible, in some cases, to derive empirical equations which cover the data very closely between the two extremes covered by Raoult's and Henry's Laws. These empirical equations are frequently of considerable value in vapor pressure calculations.

CHAPTER VII

CONCENTRATED SOLUTIONS

Mixtures of certain liquids, especially mixtures of substances which are closely related chemically, for instance, substances in the same homologous series, as benzene and toluene, follow Raoult's Law very closely, so closely, in fact, that it is possible to derive the boiling-point curve of such mixtures from Raoult's Law with a very small percentage error.

Vapor-pressure Curves for Benzene-toluene.—Figure 12 shows the vapor-pressure curves of benzene and toluene between the temperatures of 60° and 110° C. It is possible to derive empirical equations based on the Clapeyron equation which will represent these vapor pressure curves very closely.

The diagram on Fig. 13 shows the total pressure and partial pressure of benzene-toluene mixtures at different temperatures. For instance, the vapor pressure of pure benzene at 100°C. is 1,344 mm. The vapor pressure of pure toluene at 100°C. is 560 mm. On the diagram on Fig. 13, the vapor pressures in millimeters are plotted as ordinates and the mol percentages of benzene are plotted as abscissæ. (A mixture containing 30 mol per cent benzene is a mixture of 30 molecular weights of benzene and 70 molecular weights of toluene. Zero mol per cent benzene is equal to 100 mol per cent toluene.) The pressure of pure toluene, therefore, is plotted on the left-hand side of the diagram and the pressure of pure benzene is plotted on the right-hand side of the diagram, and a straight line, *AB*, is drawn, connecting these two pressures. A straight line is also drawn connecting the vapor pressure of pure toluene with a point representing 0 mol per cent toluene, and 0 mm. pressure, shown by dotted line *AC*. In the same way, a line, *BD*, is drawn connecting the vapor pressure of pure benzene and the point representing 0 per cent pure benzene and 0 mm. pressure. From Raoult's Law, any point on the line *AC* represents the partial pressure of toluene in a mixture of benzene and toluene for any given composition. Thus, a solution containing 50 mol per cent toluene will have a partial pressure for the toluene of 280 mm. In the same way, *DB* represents the partial pressures of benzene in the same mixture and a mixture containing 50 mol per cent of benzene will have a partial pressure for the benzene of 673 mm.

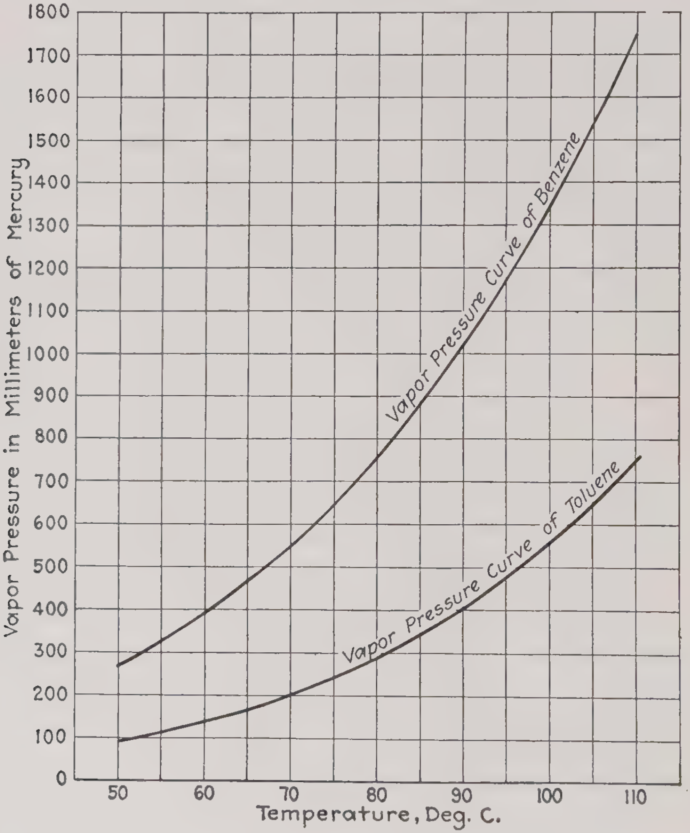

FIG. 12.—Vapor pressure curves of benzene and toluene.

Since the total pressure on the system is the sum of the individual partial pressures, the total pressure above such a mixture at 100°C. will be the sum of the two partial pressures or 953 mm. This total pressure is shown graphically by the straight line, *AB*. In the same way, the total pressures and partial pressures of mixtures of benzene and toluene can be drawn for different temperatures, and Fig. 13 indicates such lines for temperatures from

60° to 110.4°C. The partial-pressure lines for the benzene have been omitted from the diagram since the partial pressure of the benzene can be obtained by subtracting from the total pressure, the partial pressure of the toluene, lines of which are indicated.

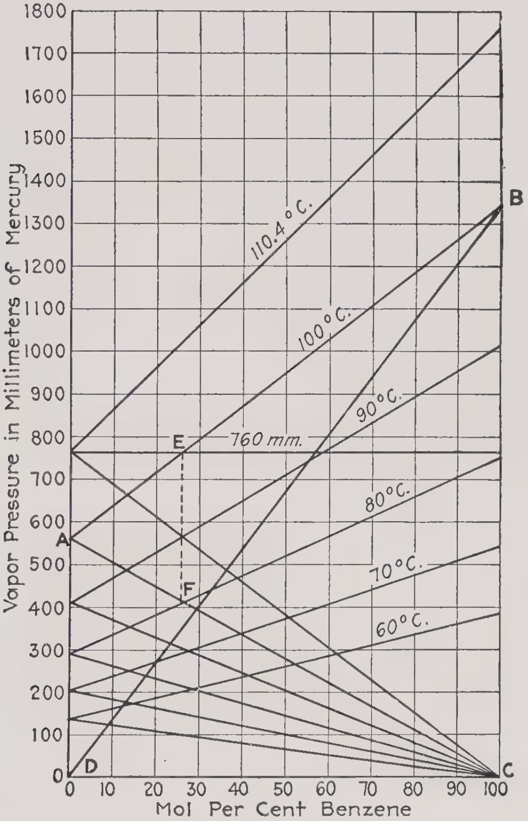

FIG. 13.—Partial pressure curves of benzene—toluene mixtures.

Distillation of Benzene-toluene Mixtures.—Suppose, now, that the distillation of a benzene-toluene mixture is being conducted at a total pressure of 760 mm. The pressure corresponding to 760 mm. is indicated on Fig. 13 and it will be noted that it cuts total pressure line at 110.4°C. at 0 mol per cent benzene, at 100°C. 26 mol per cent benzene and at 90°C. 58 mol per cent benzene.

In other words, mixtures of these three compositions will have a total pressure of 760 mm. at the respective temperatures. Thus, these mixtures will boil at these temperatures under an external pressure of 760 mm.

Boiling-point Curve for Benzene Toluene.—Fig. 14 shows the boiling-point curve of benzene, toluene mixtures at 760 mm. pressure, constructed from this data. Several intermediate points have been taken in order to determine the curve exactly. This boiling-point curve is indicated by the line *ACB*, where mol per cents benzene are plotted as abscissæ, as before, and temperatures in degrees Centigrade are plotted as ordinates. This diagram is one of constant pressure and corresponds exactly to the Phase Rule Diagram discussed previously. Any point on the line *ACB*, therefore, indicates the boiling point of any composition at 760 mm. pressure. The partial pressure of toluene at 100° over a liquid boiling at this temperature at 760 mm. is found to be 415 mm. as determined by the intersection of the dotted line *EF* (Fig. 13) with the partial pressure line *AC*, point *E* being taken where the chosen temperature cuts the total pressure line, 760 mm. This means that over a solution containing 25.7 mol per cent of benzene, at 100°C., the partial pressure of toluene is 415 mm. Therefore, the partial pressure of the benzene will be the difference of 760 and 415 mm. or 345 mm. Since the mol fraction of substances in the vapor state is proportional to the partial pressure, the mol fraction of toluene in the vapor above this solution will be equal to $\frac{415}{760} = 0.546$. In the same way, the mol fraction of toluene in the vapor above a number of solutions of these two substances which boil at 760 mm. pressure can be determined and some are tabulated in the following table.

Temperature	Composition of the liquid	Partial pressure of toluene	Mol fraction of toluene
105	12.5	567	0.746
100	25.7	415	0.546
95	40.3	285	0.375
90	58.	173	0.228
85	77.	85	0.112

Vapor Composition Curve.—It is now possible to construct a curve showing the composition of the vapor in equilibrium with any mixture of benzene and toluene boiling at 760 mm. pressure and such a curve will be found to have the form *ADB* in Fig. 14. The two curves meet at two points, *A* and *B*, the boiling points of toluene and benzene respectively. Therefore, the point *E* on the liquid line *ACB* indicates that a mixture containing 26.5 mol per cent of benzene will boil at 99.7°C. at 760 mm. pressure and the vapor in equilibrium with it will have the composition indicated by the point *F* at this temperature or 46.5 mol per cent benzene. As was pointed out before, if such a vapor were condensed it would boil at a temperature corresponding to the point *G* and would itself produce a vapor at some temperature corresponding with the point *H*. The relative ease of separating mixtures of benzene and toluene by the fractional distillation, therefore, may be indicated by the number of steps which would be required to pass from the point *A*, pure toluene, to the point *B*, pure benzene and in this case require approximately 14 or 15 such steps. It is obvious, of course, that it is impossible to produce absolutely pure *A* and *B* by such a process.

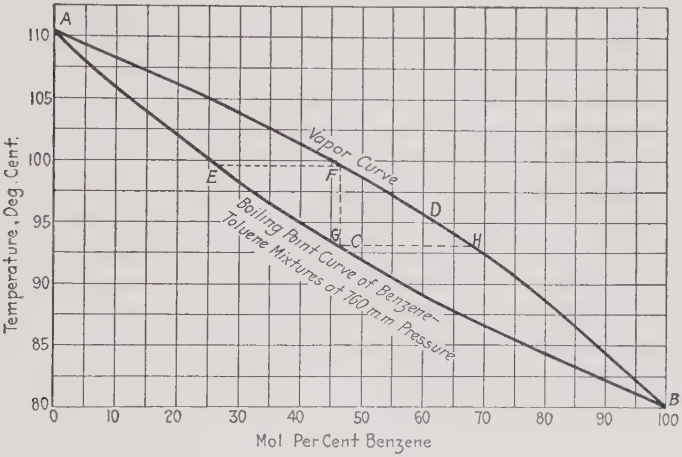

FIG. 14.—Boiling point curve for benzene-toluene mixtures.

Distillation Calculations.—It will be of advantage to calculate the quantity of liquid which must be distilled from a mixture in order to change the composition from one point to another. This may be done graphically by the aid of Fig. 14. For instance, starting with 100 mols of a mixture containing 65 mols of benzene and 35 mols of toluene, the boiling temperature will be found from the diagram to be 87.9°C. Suppose such a mixture be distilled until the temperature has risen 1°C. or 88.9°C. The composition of the liquid boiling at this temperature, from the diagram, is 61.5 mol per cent benzene, and the composition of the vapor in equilibrium with it at this temperature is 79.2 mol per cent benzene.

Between short temperature ranges, two curves, *ACB* and *ADB* may be taken to be straight lines. Therefore, the average composition of the distillate which is taken off between these two temperatures will be the average of the two extremes, 79.2, the final percentage and 82.1, the initial percentage, or 80.7.

Let x equal the mols of benzene distilled and
y equal mols of toluene distilled.

$\frac{x}{x+y}$ will be the average mol fraction of benzene in the distillate, which is equal to 0.807 and

$\frac{65-x}{65-x+35-y}$ = the mol fraction of benzene in the residue which is 0.615. This gives us two simultaneous equations, and solving for x and y we obtain

$$x = 14.7$$
$$y = 3.51$$

The total distillate, then, will be the sum of these two or 18.21 mols, leaving behind in the residue 81.79 mols which will have the composition 61.5 mol per cent benzene.

Calculation of Boiling-point Curve from the Clapeyron Equation.—The boiling-point curve at constant pressure of two liquids whose mixtures follow Raoult's Law may be estimated algebraically in the following manner.

The vapor-pressure curve of each liquid is represented over short temperature ranges by the integrated form of the approximate Clapeyron equation

$$\ln p_0 = -\frac{L}{RT} + k$$

and the partial pressure of each component over the mixture by Raoult's Law

$$p = p_0 x_0$$

where p is the partial pressure, p_0 the vapor pressure and x_0 the mol fraction of the pure component at the temperature T

$p_0 = e^{\left(-\frac{L}{RT} + k\right)}$ where e is the base of the Napierian logarithms or 2.718

$$p = xe^{\left(-\frac{LR}{T} + k\right)}$$

If x is the mol fraction of the component (1), then 1 − x is the mol fraction of the component (2), and since the total pressure is the sum of the two partial pressures

$$P = p_1 + p_2 = xe^{\left(-\frac{L_1}{RT} + k_1\right)} + (1 - x)e^{\left(-\frac{L_2}{RT} + k_2\right)}$$

where P is the total pressure, a constant.

This equation contains two variables, x and T, and if either be fixed, it is possible to solve for the other. If T is known, the solution for x is simple. The solution for T when x is given, is, however, subject to approximation, as follows:

$$P = xe^{\left(-\frac{L_1}{RT}\right)}e^{k_1} + (1 - x)e^{\left(-\frac{L_2}{RT}\right)}e^{k_2}$$

e^{k_1} and e^{k_2} are constants and can be designated as *a* and *b* respectively. $e^{\left(-\frac{L}{RT}\right)}$ may be designated as e^{-y} which when expanded as a series gives

$$e^{-y} = 1 + (-y) + \frac{(-y)^2}{2} + \frac{(-y)^3}{6} + \text{etc.}$$

substituting, neglecting powers higher than the second:

$$P = xa\left[1 - \frac{L_1}{R}\left(\frac{1}{T}\right) + \frac{L_1^2}{2R^2}\left(\frac{1}{T^2}\right)\right] + (1 - x)b \left[1 - \frac{L_2}{R}\left(\frac{1}{T}\right) + \frac{L_2^2}{2R^2}\left(\frac{1}{T^2}\right)\right]$$

collecting like terms

$$o = [-P + b + x(a - b)] - \frac{1}{RT}[bL_2 + x(aL_1 - bL_2)] + \frac{1}{2R^2T^2}[bL_2^2 + x(aL_1^2 - bL_2^2)]$$

where if x be given, the equation is in the form of a quadratic equation, and may be solved as such.

Since, however, $\frac{1}{T^2}$ is a very small quantity, the second power may be safely dropped and the equation becomes

$$o = [-P + b + x(a - b)] - \frac{1}{RT}[bL_2 + x(aL_1 - bL_2)]$$

which is a first power equation in both x and T. A further simplification is often possible, when L_1 is nearly equal to L_2 and an average value is taken for both:

$$o = [-P + b + x(a - b)] - \frac{L}{RT}[ax + b(1 - x)]$$

$$\therefore T = \frac{L[ax + b(1 - x)]}{R[-P + b + x(a - b)]}$$

It will be found, however, that the use of this equation requires very precise data since the results are obtained from differences, and the use of the experimentally or graphically determined boiling point curves are therefore preferable.

Mixtures of volatile liquids do not as a rule follow Raoult's Law completely, and the variations are very irregular.

CHAPTER VII

SIMPLE DISTILLATION

If a mixture of two volatile liquids is distilled, the distillate contains a greater proportion of the more volatile material than the residue, and as the distillation proceeds both distillate and residue become poorer in the more volatile component. This change in composition may be estimated quantitatively if the relation of the composition of the vapor to that of the liquid in equilibrium with it be known. As has been indicated above, the theoretical relations are usually difficult to handle, and empirically determined relations are frequently of value.

The Distillation Equation.—Starting with a mixture of $\overline{W}$ parts of a mixture of A and B, containing a parts of A and $\overline{W} - a$ parts of B, the composition of the liquid will be $\frac{a}{W}$ with respect to A, and the composition of the vapor will be some function of the composition of the liquid $F\left(\frac{a}{W}\right)$ or $F(x)$. Allow a differential amount $d\,\overline{W}$ of the mixture containing a differential amount of A, da, to be evaporated; there will remain as a residue $\overline{W} - d\overline{W}$ parts of mixture containing $a - da$ parts of A, and the composition of the distillate will be $\frac{da}{dW}$. Therefore $F(x) = \frac{da}{dW}$ or $F(x) = \frac{d(Wx)}{d\overline{W}}$. Simplifying this equation as follows:

$$\frac{\overline{W}dx + xd\overline{W}}{d\overline{W}} = F(x)$$

$$\frac{\overline{W}dx}{d\overline{W}} = F(x) - x$$

$$\int_{W_o}^{\overline{W}} \frac{d\,\overline{W}}{W} = \int_{X_o}^{X} \frac{dx}{F(x) - x}$$

$$\ln \frac{\overline{W}}{W_o} = \int_{X_o}^{X} \frac{dx}{F(x) - \overline{x}}$$

The solution of the problem requiring the value for $\overline{W}$ when the composition of the liquid has reached the value x can then be found by evaluating this integrated equation. In order to do this there are several methods which may be followed. First, for small temperature and composition ranges the relation between the vapor and liquid may be approximately represented by a straight line, or $F(x) = cx$, where c is some constant.

$$\text{In}\,\frac{\overline{W}}{\overline{W}_o} = \int_{x_o}^{x} \frac{dx}{cx - x} = \int_{x_o}^{x} \frac{d\,x}{x(c - 1)} = \frac{1}{c - 1} \ln \frac{x}{x_0}$$

clearing of logarithms

$$\frac{\overline{W}}{\overline{W}_o} = \left(\frac{x}{x_o}\right)^{\frac{1}{c-1}} \text{ or } \frac{x}{x_o} = \left(\frac{\overline{W}}{\overline{W}_o}\right)^{c-1}$$

Acetic Acid–Water.—The following data was taken from Lord Rayleigh,[1] giving the relation between the liquid and the vapor for mixtures of Acetic Acid and water.

Composition of liquid (x)	Composition of vapor (y)	c
0.0677	0.0510	0.75
0.1458	0.1136	
0.2682	0.2035	0.76
0.3746	0.2810	
0.4998	0.3849	0.77
0.6156	0.4907	
0.7227	0.6045	0.84
0.8166	0.7306	
0.9070	0.8622	0.95

This indicates that for values of x up to 50 per cent for acetic acid, such a procedure is safe. This was shown by an experiment as follows:

$\overline{W}_0 = 1{,}010$ grams $x_0 = 0.0757$ (7.57 per cent)

$\overline{W} = 254$ grams   Assume $c = .75$

$\left(\frac{254}{1{,}010}\right)^{0.75-1} = \frac{x}{0.0757}$ $x = 0.107$ (10.7 per cent.)

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[1] Phil. Mag., 1904, p. 534.

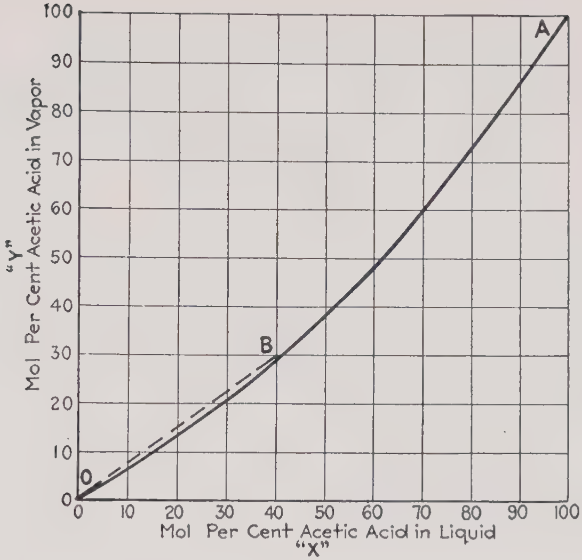

FIG. 15.—Liquid-vapor composition curve for acetic acid-water mixtures.

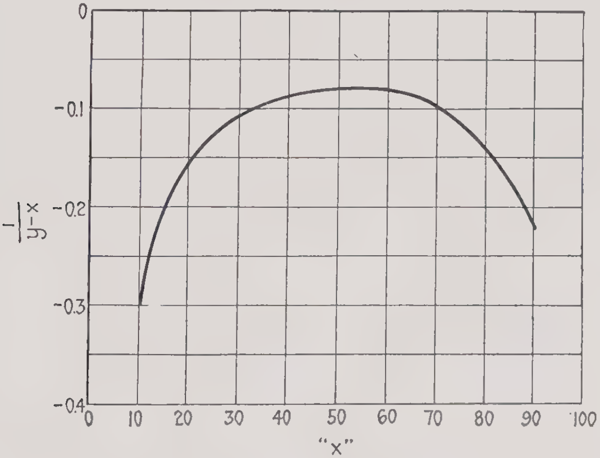

FIG. 16.—Plot of $\frac{1}{y - x}$ versus x

The actual experiment showed $x = 0.110$ (11.0 per cent) which indicates the reliability of this method.

The second method consists in finding an empirical equation for F(x). Construct a diagram as on Fig. 15, with composition of the liquid as abscissæ and composition of the vapor as ordinates, and construct a curve *OA* from the data as given in the above table. The straight line *OB* represents the $F(x) = 0.75x$ as used above. This data is of such a nature that it is not possible to fit one equation to the entire line, as it consists substantially of one curved section and one straight section. In this particular case the equation for the straight section will be as before $y = 0.75x$, while the curved section will have the form $y + a = c(x + b)^n$ where a, b, c and n, are constants which can be evaluated from data. It will be seen, however, that such an equation would be difficult to handle, and where precise results are required over a wide range it is better to use the third, or graphical method.

Construct a plot of $\frac{1}{y - x}$ as ordinates and values of x as abscissæ, as on Fig. 16. The measurement of the area under the curve between any two limits of x will therefore be the evaluation of the integral

$$\int_{x_1}^{x_2} \frac{dx}{F(x) - x} \text{ and will be equal to } \mathrm{Ln} \frac{W_2}{W_1}.$$

Simple Condensation.—The relation between the weight of a mixture distilled and its composition derived above was based on the assumption that the portion distilled was removed from contact with the liquid immediately, so that equilibrium could not be established afterwards. It is possible to condense vapor in the same way, removing the condensate from contact with the Vapor as rapidly as it is formed. Analysis of this process leads to similar equation for the relation between the composition of the vapor and the weight condensed.

$$\mathrm{Ln} \frac{W}{W_0} = + \int_{y_0}^{y} \frac{dy}{y - x}$$

where W represents the weight of the vapor and y and x the compositions of the vapor and condensate respectively.

CHAPTER IX

FRACTIONATION

The separation of two liquids from each other by fractional distillation may be accomplished in two general ways: first, the batch or intermittent method; and second, the continuous method. In the former method the composition and temperature at any point in the system are changing continually, while in the latter, conditions at any point are constant. The latter method is, therefore, the easier to treat from a theoretical standpoint and will be taken up first.

It will be recalled that a fractionating column consists of a system up through which vapors are passing, and down through which a liquid is running, countercurrent to the vapor, the liquid and vapor being more or less in intimate contact with each other. Furthermore, the vapor and liquid should be in equilibrium with each other at any point in the column, the liquid and vapor at the bottom of the column being richer in the less volatile component than at the top. It is evident, therefore, that the action of such a column is similar to that of a scrubbing or washing column, where a vapor is removed from a gas which is passing up through the column, by bringing into contact with it, counter current, a liquid in which the vapor is soluble, and which will remove it from the gas. It will be advantageous to study the action of fractionating columns from this standpoint.

Lewis' Analysis.—The following analysis, is due to W. K. Lewis.[1] With it, it is possible to predict best operating conditions for fractionating columns and it gives a rational basis for comparing their relative efficiencies. Assume a column of the type indicated by the sketch (Fig. 17).

A represents any suitable type of column, either of the plate or filled type, whose effective length is *C*. *B* represents a condenser, which condenses all of the vapors leaving the top of the column, returning part of the condensate as reflux and delivering the remainder to a receiver as distillate. The column receives $\overline{V}_o$ mols of vapor per unit time from some other part of the still, which is fed continuously with a liquid of uniform composition x_o which when vaporized delivers the vapor $\overline{V}_o$ which has the composition y_o, where x is the mol fraction of the more volatile constituent in the liquid and y, that in the vapor. The reflux R_o, returning from the bottom of the column to the source of vapor, has the composition x_1. The column delivers from the top to the condensers $\overline{V}_t$ mols of vapor per unit time, of the composition y_c, R_c mols of which are returned to the column, and $\overline{V}_c$ mols of which are withdrawn as distillate, both reflux and distillate having the same composition $x_c = y_c$.

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[1] J. Ind. Eng. Chem., I. p. 522 (1909).

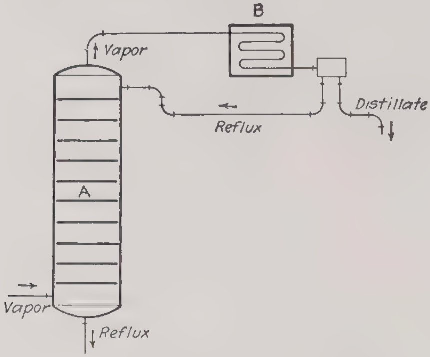

FIG. 17.—Diagram of fractionating column.

It is evident that equating input and output of the column

$\overline{V}_o = \overline{V}_c + R_o$ for the whole system and (1)

$\overline{V}_o y_o = \overline{V}_c y_c + R_o x_1$ for the more volatile component. (2)

Combining these two equations and solving for x_1

$$x_1 = y_0 - \frac{\overline{V}_c(y_c - y_0)}{R_0} \tag{3}$$

Considering a source of feed to the still of the fixed composition x_0, the vapor in equilibrium with it, y_0, is constant. Furthermore, if the quantity and composition of the distillate $\overline{V}_c$ and y_c respectively are fixed, then x_1, the composition of the reflux from the base of the column is dependent upon the size of

R_0, the amount of this reflux. If R_0 is large, the term $\dfrac{\overline{V}_c(y_c - y_0)}{R_0}$ is small, and x_1 approaches y_0 in value. In other words, the greater the amount of reflux, other things being equal, the more nearly will the composition of the reflux approach that of the vapor entering the bottom of the column. Conversely, the smaller the value of R_0, the smaller the value of x_1. Its minimum value is, of course, the composition of the entering feed, x_0.

Solving the previous equation for R_0

$$R_0 = \frac{\overline{V}_c(y_c - y_0)}{(y_0 - x_1)} \tag{4}$$

V_c, the weight of distillate from the still, will be greatest when there is no reflux, or when $R_0 = 0$. Under these circumstances, no fractionation would occur in the column, and while the thermal efficiency would be a maximum, the fractionating efficiency would be zero. This is indicated by the equation, since when $R_0 = 0$, and $\overline{V}_c$ is a finite quantity, $(y_c - y_0)$ must equal zero. In the case of the total condensation being returned to the column, R_0 is a maximum and $\overline{V}_c = 0$. The equation is then indeterminate, but differentiating with respect to R_0 and x_1 gives:

$$\frac{dR_0}{dx_1} = \frac{\overline{V}_c(y_c - y_0)}{(y_0 - x_1)^2} \tag{5}$$

which, since y_c is greater than y_0, is a positive differential, and indicates that R_0 increases with x_1, and, therefore, has its maximum, value when x_1 is a maximum or when $x_1 = y_0$ and has its minimum when x_1 is a minimum, or when $x_1 = x_0$.

Thermal Efficiency.—It is possible to calculate the thermal efficiency of a column, based upon the fact that a perfect column is one which returns a minimum of reflux to the source of vapor, which occurs when $x_1 = x_0$. This means that, if separation occurs in the column, the change in composition between the source of vapor and the bottom of the column must be a differential quantity only, and that the change throughout the column must be differential also. Therefore, in the ideal column obtained

$$\overline{V}_0 = \overline{V}_c \frac{(y_c - x_0)}{y_0 - x_0} \tag{6}$$

by combining equations (1) and (3) and making $x_1 = x_0$. In the ideal column $\frac{\overline{V}_0}{\overline{V}_c} = \frac{y_c - x_0}{y_0 - x_0}$, while in the actual column, $\frac{\overline{V}_0}{V_c} = \frac{y_c - x_1}{y_0 - x_1}$. The thermal efficiency will therefore be

$$\frac{y_c - x_0}{y_0 - x_0} \div \frac{y_c - x_1}{y_0 - x_1} \text{ or } \frac{(y_c - x_0)\,(y_0 - x_1)}{(y_0 - x_0)\,(y_c - x_1)} \tag{7}$$

Column Insulation.—Working against thermal efficiency is separation efficiency. At any section of the column, n, the composition of the reflux (x_n) to a lower point of the column n $- \Delta$ n, is a function of the concentration of the vapor (y_n) at the section n. It is evident, then, that the separation in the column between the sections n $-$ Δn and n will be greater, the greater the difference between x_n and $y_{n-\Delta n}$. In other words, for a given value of the latter, the former should be as large as possible. Equation (3) may be written

$$x_n = y_{n-\Delta n} - \frac{\overline{V}_c(y_c - y_{n-\Delta n})}{R_{n-\Delta n}} \tag{8}$$

Since x_n will be the greater, the greater the value of $R_{n-\Delta n}$, the fractionation in the column will be the greater, the greater the amount of reflux. This very important conclusion should lead to the complete insulation of the fractionating column against heat losses to the outside, in order to prevent condensation occurring in the column itself, as maximum efficiency of separation will occur when the reflux is a maximum throughout the column. The best column should have its reflux entirely in the condenser above the column, and the entire reflux returning through the entire length of the column.

CHAPTER X

RATE OF FRACTIONATION[1]

The height of a fractionating column or the number of plates required will be less, the greater the ratio of reflux to distillate. Conversely, the greater the number of plates, the less becomes the necessary reflux ratio. For an infinite number of plates, there will be a definite minimum reflux ratio, below which it is not possible to obtain the desired fractionation.

Lewis's Method.—From Eq. (4) there may be written for any plate, n, per unit time.

$$R_{n+1} = \overline{V}_c \frac{y_c - y_n}{y_n - x_{n+1}} \tag{9}$$

and the minimum value for R_{n+1} will be obtained when the fractionation from one plate to the next approaches zero, or when $x_n = x_{n+1}$. For the n_{th} plate, therefore, the minimum reflux, R^1_{n+1}, will be

$$R^1_{n+1} = \overline{V}_c \frac{y_c - y_n}{y_n - x_n} \tag{10}$$

The rate of increase in concentration of the liquid in the column from one plate to the next may be expressed by the differential, $\frac{dx}{dn}$; therefore,

$$x_{n+1} = x_n + \frac{dx}{dn} \tag{11}$$

If, for purposes of simplification $V_c = 1$, then combining Eqs. (9) and (11) gives

$$R_{n+1} = \frac{y_c - y_n}{y_n - x_n - \frac{dx}{dn}} \text{ or} \tag{12}$$

$$\frac{dx}{dn} = (y_n - x_n) - \frac{1}{R_{n+1}}(y_c - y_n) \tag{13}$$

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[1] W. K. Lewis (not yet published).

Equation (13) gives the theoretical rate of concentration per plate in a fractionating column when conditions are perfect. Since columns are not 100 per cent efficient, the actual rate of concentration will be something less than the theoretical, it being assumed that the ratio $\frac{dx}{dn}$ (actual) $= k\frac{dx}{dn}$ (theoretical). Equation (13) then becomes

$$\frac{dx}{dn} \text{ (actual)} = k(y_n - x_n) - \frac{k}{R_n + 1}(y_c - y_n) \qquad (14)$$

This equation means that the rate of fractionation in a column is determined by five things: First, the efficiency of the column, k; second, the ratio of reflux to distillate, R; third, the composition of the liquid on any plate, x_n; fourth, the composition of the vapor above the liquid on the n^{th} plate, y_n, and fifth, the composition of the distillate, y_c.

The reciprocal of $\frac{dx}{dn}$, that is, $\frac{dn}{dx}$, when integrated between any two limits of x, gives the actual number of plates which will be required providing *k* and *R* are known and y_c, the composition of the distillate required, has been determined. Where columns of the filled type are used, and no plates are present, the same equation is applicable, the symbol *n* indicating some unit of length of the column, such as the foot. Thus, for a filled type column 16 ft. high, n would be 16, and $\frac{dx}{dn}$ would represent the change in composition of the liquid per foot of height of the column.

Illustration of Method of Lewis.—In order to illustrate the use of this method of calculating column sizes, the case of the separation of water and acetic acid will be considered.

The relation between the vapor and liquid compositions for acetic acid (HA_c) and water have been determined by Lord Rayleigh[1] (see page 46). In order to make use of this data, it is necessary to convert it from weight per cent to mol per cent. This has been done, making use of the apparent molecular weight of acetic acid vapor (approximately 104 as determined by the vapor density) instead of the formula weight (60), since it is necessary to have an equal number of mols of vapor, or reflux, passing all points of the column at any given instant, and the molal heats of vaporization of the two components must be approximately equal. In most cases, the formula weight is the same as the molecular weight, as in the case of water, ethyl alcohol, benzene and others. In such cases the formula weights are used in constructing the mol per cent chart. Acetic Acid, and a few other substances are unusual in this respect. Under these conditions R is the same at all points in the column. The resulting y *vs.* x curve is given in Fig. 18.

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[1] Phil. Mag., (6) 4 (1902), p. 521.

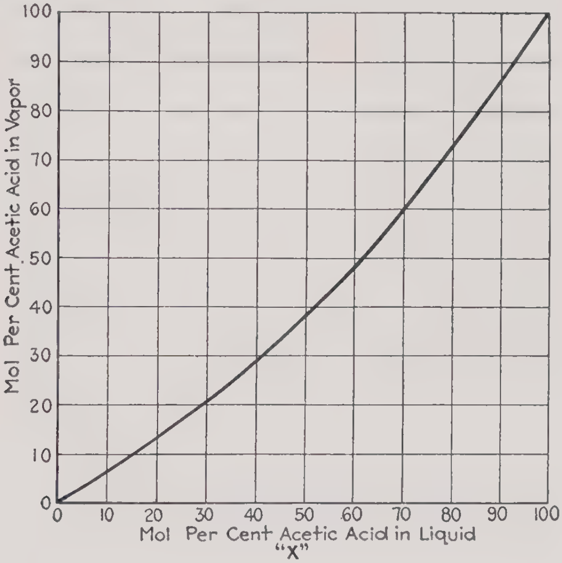


Fig. 18.—Vapor composition curve for acetic acid-water mixtures.

Let there now be assumed a definite problem: To calculate the number of plates and the reflux ratio, required to fractionate a 40 per cent acetic acid solution, delivering a distillate of 12 per cent, and leaving a residue containing 80 per cent.

Continuous Still.—The operation may be carried out by means of a continuous still or by means of an intermittent one. The case of the continuous still will be considered first.

In Fig. 19 *A* represents the column of a continuous still with the feed liquor (40 per cent) entering boiling hot at some undetermined point. Heat for vaporization is supplied by some suitable heating device *B*, the residue (80 per cent) leaving the bottom of the column at this point. The vapor passes to the condenser *C*, part of the condensate returning to the top of the column while the balance is drawn off as distillate at *D* (12 per cent).

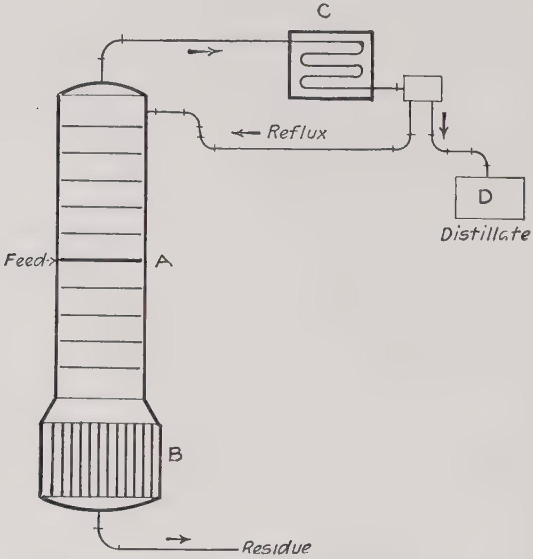


FIG. 19.—Diagram of continuous still

The operation of the column in a continuous still is complicated by the fact that while the number of mols of vapor passing up through the column per unit of time is the same for all portions of the column, the number of mols of reflux passing in the opposite direction is increased at the feed plate by the addition of the entering feed. Thus for a reflux ratio above the feed plate of R_{n+1}, the reflux ratio below the feed plate (R_{m+1}) will be greater than R_{n+1} by the amount of feed per mol of distillate, R_f.

$$R_{m+1} = R_{n+1} + R_f \tag{15}$$

Equation (14) will, therefore, not apply directly in a continuous column to the portion below the feed plate, but a similar one

$$\frac{dx}{dm} = k(y_m - x_m) - \frac{k(R_f - 1)}{R_{m+1}}(y_m - x_w) \tag{16}$$

making use of the concentration of the liquor leaving the bottom of the column (x_w) may be substituted for it. In this equation *m* has the same significance as *n*, being used to distinguish plates below the feed plate, while *n* is reserved for plates above the feed.

The point of entrance of the feed into the column was stated to be undetermined. Realizing that at this point *m* and *n* are the same, and since there must be continuity of operation at this point, $\frac{dx}{dn}$ and $\frac{dx}{dm}$ must also be equal, then equations (14) and (16) may be equated to obtain the exact concentration at which the feed must enter, or

$$y_n = \frac{y_c(R_{n+1} + R_f)}{R_f(R_{n+1} + 1)} \qquad (17)$$

Furthermore the minimum reflux below the feed plate will become

$$R^1_{m+1} = (R_f - 1)\frac{y_m - x_w}{y_m - x_m} \qquad (18)$$

In the problem selected it is first necessary to determine how the *minimum* reflux changes throughout the column, in order to select an *actual* reflux which will be big enough to satisfy all points in the column. Since the feed plate has not been determined, being dependent on the as yet unselected R_{n+1}, it is necessary to calculate R^1 for the whole column on both the basis of above the feed plate and of below the feed plate.

The following calculations will be based entirely on one mol of distillate, $\bar{V}_c = 1$, and with the apparent molecular weight of acetic acid as 104.

The mol fraction of the HAc in the entering feed (40 per cent) will be

$$\frac{40}{104} = 0.385 \qquad \frac{0.385}{3.715} = 0.1036$$

$$\frac{60}{18} = \frac{3.33}{3.715}$$

That of the distillate (12 per cent) and the residue (80 per cent) calculated the same way, will be 0.0155 and 0.409 respectively. For one mol of distillate, the mols of feed, R_f, may be calculated by means of two simultaneous equations, where *a* = mols of feed, and *b* = mols of residue

$$a - b = 1.0 \qquad a = 1.287 = R_f$$

$$0.1036\,a - 0.409\,b = 0.0155 \qquad b = 0.287$$

The following table gives the calculated values of $R_n^1 + 1$ and $R_m^1 + 1$, for values of x between the limits of which the column must work, using equations (10) and (18) respectively. The values of y were read from the x − y curve on Fig. 18.

x	y	$R_n^1 + 1$	$R_m^1 + 1$
0.409	0.296	2.48	0.287
0.350	0.245	2.18	0.448
0.300	0.204	1.96	0.612
0.250	0.168	1.86	0.843
0.200	0.133	1.75	1.18
0.150	0.098	1.58	1.72
0.100	0.066	1.47	2.89
0.075	0.050	1.36	4.12
0.050	0.033	1.00	6.20
0.025	0.0165	1.18	

Since the feed plate will probably be found to be below that point where x = 0.100, a selected value for the actual reflux, R, to be used should not be less than 2.89, so a value of 3.0 will be used. In case such a selection proves too small, a larger value must be taken, and the later work repeated.

It was stated that the feed should enter at such a value of x that $\frac{dx}{dn} = \frac{dx}{dm}$. The simplest way to determine this point is to construct a curve of $\frac{dx}{dn}$ *vs.* x and one of $\frac{dx}{dm}$ *vs.* x, and the point of their intersection will give the value of x desired. Since, however, it is necessary to construct a plot of $\frac{dn}{dx}$ *vs.* x in order to obtain the integral of Eq. (14), the reciprocal of $\frac{dx}{dn}$, $\frac{dn}{dx}$, is plotted instead. The following table gives values of $\frac{dn}{dx}$ and $\frac{dm}{dx}$ for values of x, as calculated from Eqs. (14) and (16) respectively, using a value of k = 0.90.

x	y	$\frac{dn}{dx}$	$\frac{dm}{dx}$
0.409	0.296	....	−105.0
0.350	0.245	....	− 11.8
0.300	0.204	....	− 13.5
0.250	0.168	....	− 16.9
0.200	0.133	− 39.7	− 22.6
0.150	0.098	− 45.0	− 35.7
0.100	0.066	− 64.1	−101.0
0.075	0.050	− 81.3	
0.050	0.033	− 98.0	
0.025	0.0165	−136.0	

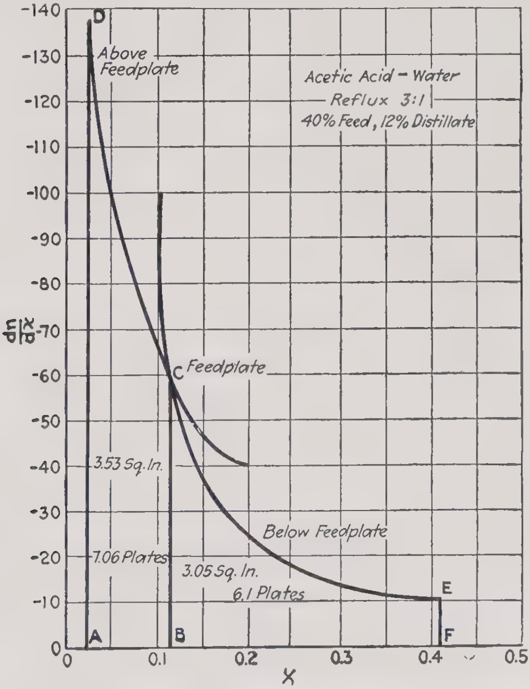


FIG. 20.—Plot of $\frac{dn}{dx}$ and $\frac{dm}{dx}$ versus x (reduced scale).

These values of $\frac{dn}{dx}$ and $\frac{dm}{dx}$ when plotted against x, as shown in Fig. 20, cross at x = 0.1125, thus giving the composition of the liquor on the feed plate, when $R = 3.0$. It should be noted that the composition of the liquor on the feed plate, and therefore the position of the feed plate, will change as the reflux ratio changes, increasing R, lowering its position, and *vice versa*.

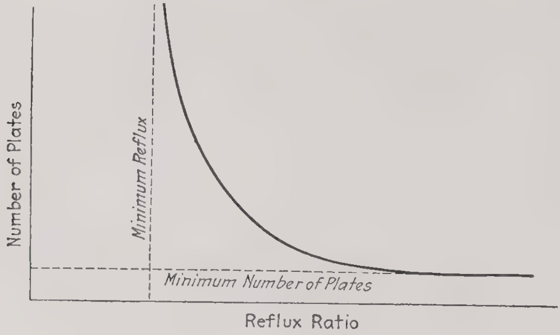


Fig. 21.—Curve showing relation between reflux ratio and number of plates.

The number of plates required in the column, both above and below the feed, may now be determined by measuring the area under the $\frac{dn}{dx}$ and $\frac{dm}{dx}$ curves. The area *ABCD* gives the number of plates above the feed (7.06 plates or 8) while the area *BCEF* gives the number of plates below the feed (6.1 plates or 7), the total number of plates required being 15.

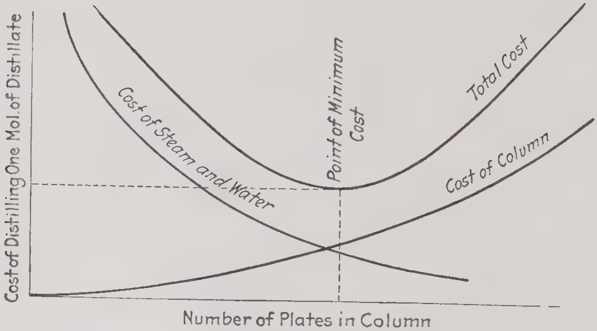


Fig. 22.—Optimum number of plates in fractionating column.

It should be noted that increasing R will decrease the number of plates until with infinite R, the number of plates will become a minimum. The change in the number of plates with the change in reflux will, in general, give a curve resembling Fig. 21.

The choice of the number of plates and the corresponding reflux actually to be used will depend upon an economic balance between the cost of the column, and the cost of steam or other heat and water for operating it. A small column will cost less, but the necessary large reflux ratio will mean a large steam and water consumption, whereas a large column, while giving a smaller heat consumption, will cost more. This may be illustrated graphically in Fig. 22.

Intermittent Still.—The use of the intermittent still in the solution of the problem of the separation of acetic acid and water requires a modification in the solution as outlined above. An intermittent still consists essentially of three parts—a kettle, a column, and a condenser, as illustrated in the above sketch. It differs from the continuous still in that a charge of a given amount of a given composition (40 per cent HAc, for instance) is placed in the kettle, distillation commences, and a distillate is removed continuously from the condenser until the residue in the kettle has reached the proper concentration (80 per cent in this particular case). During this distillation, the composition

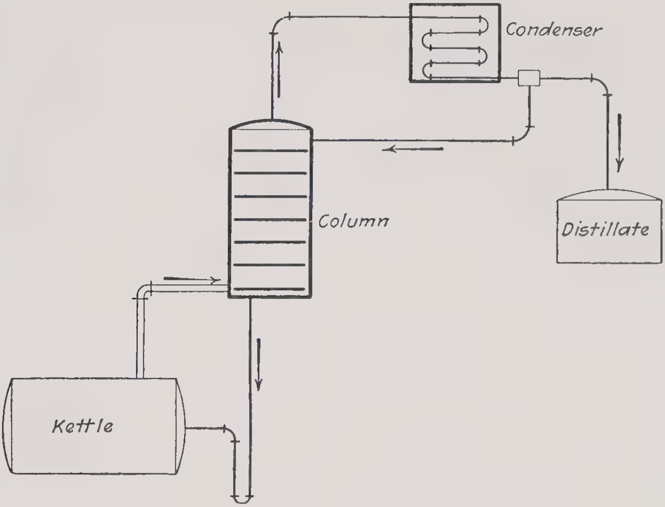


FIG. 23.—Diagram of an intermittent still.

of the charge in the kettle is continually changing, and, therefore, conditions in the column are changing also. It is possible to keep some things unchanged in such a distillation. The composition of the distillate may remain constant, and under such conditions, the ratio of reflux to distillate will constantly increase. If the rate of vaporization in the kettle remains the same, the velocity of the vapor passing up through the column will remain approximately the same, and therefore the rate of distillation will continuously decrease.

It is possible to keep the rate of distillation constant in addition to keeping the composition of the distillate constant, by continually increasing the amount of vaporization in the kettle, but this is not a preferred method of operation, since the column is not working at capacity during the first part of the run.

Assuming a constant vapor velocity in the column, the number of mols of vapor rising through it per unit time, will at any time during the run be expressed by the equation

$$V_cR + \overline{V}_c = \text{constant} \tag{19}$$

The minimum reflux R^1 at the start, if $V_c = 1$, can be calculated from Eq. (10).

$$R^1 = \frac{0.0155 - 0.0684}{0.0684 - 0.1036} = 1.51 \tag{20}$$

The number of plates needed at the start of the distillation can now be calculated by means of Eq. (14), assuming R sufficiently greater than R^1 to give a reasonable number of plates, and knowing k, the plate efficiency. Therefore let

$$R = 2.0 \text{ and } k = 0.90 \text{ as before.}$$

The following table gives the results of the calculations:

x	y	$\frac{dn}{dx}$
0.1036	0.0684	−127
0.100	0.066	−123
0.075	0.050	−143
0.050	0.033	−135
0.025	0.0165	−138
0.024	0.0155	−131

The irregularities in the values of $\frac{dn}{dx}$ are due to errors in reading the x − y curve and in using differences therefrom. This data is shown plotted as $\frac{dn}{dx}$ versus x on Fig. 24 and the integrated area under it is found to amount to 10.5 plates, the actual number required to produce 1 mol of 12 per cent HAc per unit time at the start of the distillation, when the reflux ratio is 2:1.

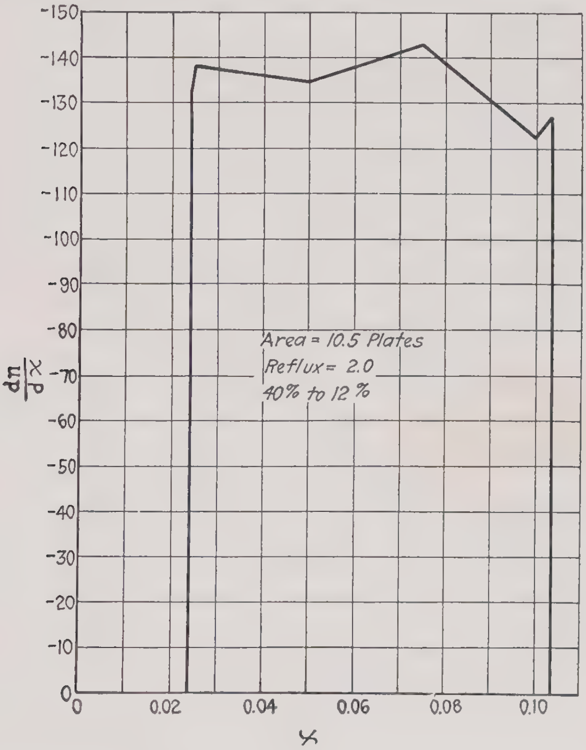


Fig. 24.—Plot of $\frac{dn}{dx}$ versus x.

The number of plates in the column having now been fixed at 10.5 (11 actual plates), and the distillation started, since the concentration of the acetic acid in the kettle is becoming greater, the value of R must increase, and the rate of distillation per unit time V_c, must decrease so that $V_cR + V_c$ = constant = 3.0.

The conditions under which the still will be operating at the end of the run will be as follows:

Composition of liquid in the kettle = 80 per cent (0.409)
Composition of distillate = 12 per cent (0.0155)
Reflux ratio, R, undetermined
Rate of distillation per unit time, $\overline{V}_c$, undetermined
Number of plates constant at 10.5
Plate efficiency assumed to remain constant at 0.90.

It is now necessary to select several values for R, and using the terminal conditions stated above, obtain a curve of the corresponding values of $\frac{dn}{dx}$ using Eq. (14). This curve will pass through the value of 10.5 for the number of plates, thus giving the reflux ratio desired. The following table gives the results of such a series of calculations.

x	y	R=2.5 $\frac{dn}{dx}$	R=2.7 $\frac{dn}{dx}$	R=2.9 $\frac{dn}{dx}$	R=5.0 $\frac{dn}{dx}$	R=7.0 $\frac{dn}{dx}$
0.409	0.2960	−100.0	−119.0	− 67.6	− 19.5	− 15.2
0.300	0.2040	− 53.8	− 42.3	− 39.3	− 19.1	− 16.1
0.200	0.1330	− 55.6	− 47.2	− 42.0	− 25.6	− 22.2
0.100	0.0660	− 80.7	− 72.3	− 67.2	− 46.5	− 41.5
0.050	0.0330	−111.0	−105.0	−101.0	− 82.0	− 76.0
0.025	0.0165	−137.0	−136.5	−136.0	−134.0	−133.0
0.024	0.0155	−131.0	−131.0	−131.0	−131.0	−131.0
Number of plates........		38.2	24.8	21.3	13.0	11.0

The curve shown on Fig. 25 is this relation between R and n (the number of plates) for the end of this distillation. It is seen that this curve cuts the value of *n* of 10.5 at R = 7.3. In other words, the ratio of reflux to distillate at the end of this distillation, using a column with 10.5 (11.) plates is 7.3:1.

Since $\overline{V}_c R + \overline{V}_c = 3.0$ and $R = 7.3$

$7.3\overline{V}_c + \overline{V}_c = 3.0$ $\overline{V}_c = 0.361$

The rate of distillation at the end will therefore be 36.1 per cent of that at the start, the composition of the distillate remaining constant at 12 per cent HAc. It is of interest to the designer of intermittent stills to be able to predict the average rate of distillation during a run. This may best be done by taking a few points between the initial and final concentrations of the liquid

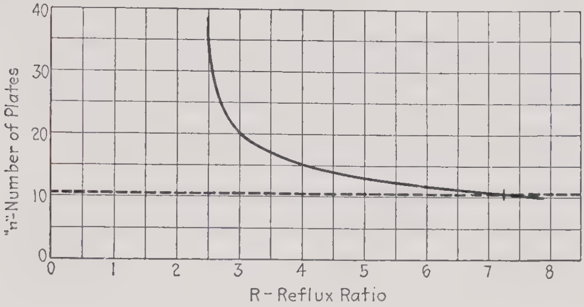


FIG. 25.—Plot of reflux ratio versus number of plates.

in the kettle and determining the proper value for R for these concentrations. It will then be possible to construct a curve of R *vs.* x_0 (kettle concentration), and determine the average value

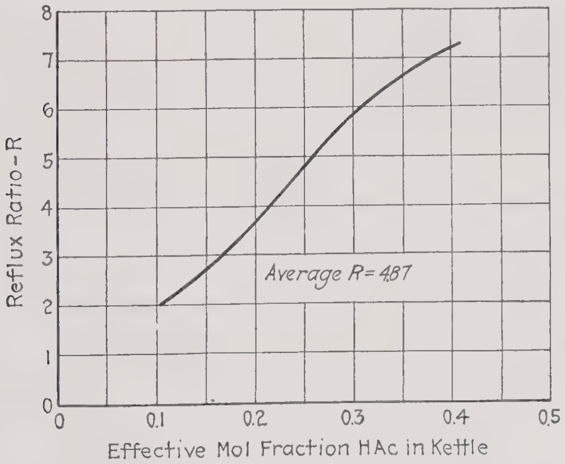


FIG. 26.—Plot of reflux ratio versus concentration in kettle.

of R by measuring the area under it. This has been done as follows:

When $x_0 = 0.300$

$R =$	2.5	2.7	2.9	5.0	7.0	$R = 5.9$ when $n = 10.5$
$n =$	19.4	17.2	15.9	11.3	9.9	

when $x_0 = 0.200$

$R =$	2.5	2.7	2.9	5.0	7.0	$R = 3.8$ when $n = 10.5$
$n =$	14.3	12.9	12.2	9.1	8.2	

These results have been plotted on Fig. 26, and the area under the curve indicates that the average value of $R = 4.87$. The average rate of distillation is calculated as before.

$$4.87\bar{V}_c + \bar{V}_c = 3.0$$

$$\bar{V}_c = 0.51$$

The average rate of distillation under these conditions will, therefore, be 51 per cent of the initial rate.

CHAPTER XI

DISCONTINUOUS DISTILLATION

It has been pointed out previously that fractional distillation may be carried out either continuously or intermittently. The continuous process takes the material to be distilled continuously at a uniform rate and delivers the products of the distillation continuously.

The discontinuous or intermittent process takes the material to be distilled in batches, each batch being completed before the next is started.

Advantages of Discontinuous Distillation.—The continuous system has the advantage that the concentration of components remains the same at any point in the system, while in the discontinuous type the concentration changes progressively with the distillation. The discontinuous type is, however, much more popular than the continuous in a great many industries, since it is frequently possible to adapt a discontinuous still designed for one purpose, for use with other materials, with a considerable degree of success, whereas the continuous type of still, when designed for a particular product and for a particular capacity, frequently must undergo considerable re-arrangement in order to use it for other purposes. Furthermore, the discontinuous stills are of simpler design and construction, considerably less expensive to install, and frequently more suitable for small scale operations, where quality and quantity of the materials to be distilled are likely to be subject to frequent change.

The discontinuous still consists, ordinarily, of three parts, the first part, which may be called the kettle, where the boiling of the charge occurs, the fractionating device, which is usually in the form of a fractionating column, and the condenser.

The Kettle.—The function of the kettle is to hold the charge to be distilled, to bring it into contact with the source of heat so that it may be vaporized, to permit disengaging space for the separation of the vapor from the liquid, and to act as a receptacle for the less volatile residual product of the distillation. The kettle is usually in the form of a tank of either horizontal or vertical cylindrical construction, the smaller sizes being vertical and the larger sizes being horizontal. On the smaller kettles, the heating is frequently done by means of a jacket surrounding the lower portion of the kettle, while on the larger vertical and on all of the horizontal types of kettles, the heating is done by means of internal coils. Where open steam is introduced in addition to the closed heat supply, a perforated sparger pipe is used in addition to the other heating surface. The kettle must be fitted with connections for introducing the charge, for dumping the distilled residue, for the passage of the vapor from the kettle to the fractionating device and for the return of the reflux from the fractionating device to the kettle. The larger sizes are also fitted with other accessories such as pressure gages, thermometers, gage glasses for determining the level of liquid in the kettle, vacuum or pressure valves, manholes and other necessary accessories.

The size of the kettle is a function of the amount of material to be handled per charge, the time in which each charge is to be distilled and the behavior of the charge during distillation, so far as foaming and excessive entrainment may occur. The heating surface required in the kettle is also a function of the amount of material which must be distilled per unit time and, in addition, is dependent upon the difference in temperature between the heating medium and the material which is being boiled, the physical characteristics of the heating medium and the charge, and a number of other factors, dependent upon the design of the kettle and the heating surface. These factors will be discussed later.

The Column.—The fractionating device, which receives the vapor from the kettle, is usually, but not necessarily, in the form of a fractionating column. The function of this device is to hold back the less volatile component of the vapor from entering the bottom of the column, allowing the more volatile component to pass off from the top to the condenser where it is to be collected as distillate. As has been noted previously, the action of the column is, to a certain extent, similar to that of a scrubbing column, where the less volatile component is scrubbed out of the vapor by a descending column of liquid known as the reflux. It is necessary, therefore, in order to obtain efficient fractionation, that the descending reflux and the ascending vapor remain in as intimate contact with each other as it is possible to obtain during any passage of the vapor up through the column. Furthermore, it is to be noted that the action of a scrubbing column of this type is essentially a countercurrent action and any designer of a fractionating column should keep this countercurrent effect in mind, since true countercurrent action in any sort of a process of heat interchange such as this, is necessary in order to obtain best results.

Furthermore, it has been pointed out that most efficient results are obtained when the quantity of reflux passing down through the column is a maximum throughout the entire length of the column. Therefore, the best type of fractionating device would be that type which depended entirely for its supply of refluxing liquid from a reflux condenser situated above the column, and which itself suffered no loss of heat and therefore intermediate condensation throughout its length.

It is the object of designers of distilling equipment to produce this intimate contact required in the fractionating column, and other things being equal, the value of each fractionating device depends upon the degree of contact which has been obtained.

Filled-type Columns.—In general, fractionating columns may be said to consist of cylindrical shells filled with distributing material which breaks the descending current of liquid up into thin streams and brings the ascending current of vapor into intimate contact with these streams. The earliest type of column, and one which is still used to a large extent, consists of a cylindrical shell filled with pieces of inert solids, usually small irregular pieces of stone, porcelain, coke and other similar materials. This type of column is similar to the fractionating device which is used in the Chemical Laboratory, which consists of a glass cylinder filled with a large number of small glass beads. This type of column is inexpensive to construct and, for many purposes, will furnish sufficiently good fractionation. It, however, tends to form channels; that is, the vapor will tend to pass up through one portion of the cross-section of the column while the liquid may tend to descend through another portion of the cross-section, thus defeating the purpose of bringing the liquid and vapor into intimate contact with each other.

In filled types of columns of this sort, channeling is, to a certain extent, overcome by using filling material of a uniform nature, such as specially made stoneware shapes which when carefully packed into the column by hand, insure even distribution of vapor and liquid. Such filled types of columns are frequently used in the distillation of acids such as nitric and sulphuric acid and are very successful for such purposes. It must be remembered, however, that even under the best circumstances, the contact between vapor and liquid in such columns is poor, and therefore they should be used only where it is a relatively simple matter to separate the more volatile from the less volatile component.

Raschig Rings.—Another variety of fractionating column of the filled type has for the filling material, small cylindrical rings or tubes, the length of each ring being equal to its diameter. These rings are known as Raschig rings from their inventor, and are rapidly displacing other types of filling material for this type of column. These rings are not packed carefully into the columns, but are dumped in, and owing to their dimensions and shape, form a fairly uniform packing with very little opportunity for liquids and gases to channel. They have the further advantage of offering a very large surface wet with the liquid and exposed to the action of the vapor and there are no pockets where liquid may be caught and held from running down.

Pressure Drop in Columns.—The filled types of columns are particularly useful where the drop in pressure through the column must be very small. The other types of columns, consisting of trays and plates holding layers of liquid, necessitate a considerable drop in pressure in order to overcome the static head of the liquid on the plates. In systems which operate under very small pressure drops such as scrubbing and washing systems, where the gas passing through the column is delivered by ventilating fans which operate under very low pressure heads, or in the case of high vacuum distillation, where a slight change in pressure would mean a considerably greater change in the temperature of the material in the still, great pressure drops must be avoided and the filled type of column, which has no static head of liquid to overcome, is the one usually selected for this purpose.

The use of filled types, however, constitutes a very special branch of distillation industry and they are not commonly found in connection with fractionating stills.

Plate Columns.—Fractionating columns are usually built up of superimposed sections separated by plates, the plates being so constructed that the vapor passes through them and comes into contact with liquid which is resting on the plate. The plates are so constructed that the reflux discharge from the plate above on to the plate below overflows from this plate by means of a suitable overflow pipe to the plate below it, while the vapor passes up from one section, through the plate, through the liquid on the plate into the next section and so on. The plates in fractionating columns differ from each other chiefly in the design of the devices by which the vapor and liquid are brought into contact with each other.

Perforated Plates.—The simplest type of plate is the perforated plate where a large number of small holes are drilled in the plate and the vapor passes up through these holes, the pressure of the vapor preventing the liquid from running down through them. There is a suitable overflow pipe for the liquid on each plate to enable it to get from one plate to the one below it. Such plates are very efficient if the holes through which the vapor passes are very small and very close together. They, however, must be operated at such a velocity that the pressure of the vapor underneath the plate is greater than the static head of liquid over the plate, in order to prevent the liquid from running back through the vapor openings. This means that such plates cannot operate successfully at less than a definite vapor velocity. Furthermore, these plates have the disadvantage that if they are operated too rapidly, the vapor tends to lift the liquid off of the plate, thus interfering with the good contact between the liquid and vapor and destroying the efficiency of the fractionation.

There is still another difficulty with these plates, which is especially true in columns of great diameter. If the plates are not perfectly horizontal, the liquid will collect at the lower side of the plate and therefore the depth of liquid at that point will be greater than at the higher side of the plate. This will mean that the static head over the lower portion of the plate is greater than that at the higher portion and since the vapor will tend to pass most rapidly through that portion of the plate where the static head is less, the result is that the vapor passes up through the higher side of the column while the liquid remains on the lower side of the column and poor contact between the liquid and vapor is obtained. Furthermore, the holes are easily clogged up with solid matter. These difficulties with the perforated plate type of column have gradually led to its abandonment in most industries. It is, however, retained in certain industries which will be mentioned later.

Perforated Plates for Suspensions.—The next improvement in the plate type of column consisted in forming a lip over the perforations in the perforated type column so that the vapor passing through the perforation, instead of rising vertically through the liquid above, was directed horizontally by the lip over the hole, so that it spread itself into more or less of a thin sheet of vapor before rising through the liquid, and therefore came into much more intimate contact with the liquid. This design has been found to be much more efficient than the perforated plate type on this account. It has the added advantage that if there are solids in suspension in the liquid passing down through the column, the high velocity of vapor passing out under the lip tends to keep the plate scoured clean around the opening. This is particularly advantageous in the distillation of brewery mashes and similar mixtures. This type has, however, the other objections of the perforated plate design.

Bell-type Plates.—The next improvement in the plate type of column consisted in forming a permanent seal of liquid on each plate. This was done by placing rings around the holes through the plate so that the liquid could not fall below the level of the upper edge of these rings. Covers were then placed over the rings, the edges of which dipped down under the surface of the liquid. The vapor passing up through the plate over the top of the ring, had to pass under the edge of the cover; in other words, it had to bubble through the liquid in order to escape into the space above.

The earliest designs of this type had a relatively small number of long rectangular slots on each plate, the slots covered with long covers of the same shape. A cylindrical column would frequently have four such slots, two long ones and two short ones. The area of contact of liquid and vapor, therefore, could be taken substantially as the sum of the perimeters of the rectangular covers on the plate, and the capacity of the column would be a function of this area of contact.

Another design which was frequently seen had instead of several rectangular openings in the plate, one large circular opening in the center covered with a large circular cap, dipping down into the liquid surrounding the opening. The edges of this cap were frequently made serrated to furnish a greater surface of contact between the liquid and the vapor. The serrated edges assisted in breaking up the large bubbles of vapor which escaped up into the liquid, into a number of smaller ones, and increased the area of contact to a considerable degree. Since, however, the capacity and efficiency of fractionating columns depends upon the intimate contact of vapor and liquid, it was realized that if instead of a few large openings in the plate, a large number of smaller openings were employed, this area of contact would be much increased and therefore modern design has adopted the so-called cap-type plate and it is used almost exclusively in nearly all industries.

Modern Cap-type Columns.—This cap type consists of a relatively large number of small caps over suitably spaced openings in the plate, the liquid being prevented from running down through these openings by suitable rings, the edges of the caps being sealed in the liquid.

Another improvement which has done much to increase the efficiency of the plates has been the cutting of slots in the sides of the caps underneath the surface of the liquid, so that the vapor would pass out through the slots instead of bubbling out underneath the edge of the cap. By making these slots fairly small and cutting a large number around each cap, the area of contact between the vapor and the liquid has been increased to a very great extent and the consequent capacity of the column increased in like proportion. The most up-to-date designs of fractionating stills invariably use this type of column.

Overflow Pipes.—The liquid running down through the column must be supplied with suitable overflow pipes so that it will flow from one plate to the one below it, and these may be either internal or external. The internal overflow pipes consist of tubes projecting through the plate to a definite level above the plate and the level of liquid on the plate is determined by the height of the projection of this overflow pipe above the plate itself. The pipe then passes down to the plate below and discharges underneath the level of liquid on the lower plate, thus being sealed against passage of vapor through it in the opposite direction.

The external overflow pipes withdraw the liquid from the side of the column and deliver it underneath the level of liquid on the plate below. The external type have very little advantage for most work and have been gradually displaced by the internal downpipe design.

Usually, the overflow from one plate is diametrically opposite the overflow from the lower plate to the one below it, so that the liquid running onto the plate at one point, flows diametrically across the plate to the overflow pipe, thus tending to bring the liquid into contact with a greater proportion of the area of the plate. In large columns, however, it is questionable if the portions of the plate at right angles to the center of the diameter, representing the flow of liquid from one downpipe to the next, receive as much of the liquid as they should. In other words, there is the opportunity for the liquid to short-circuit directly across the plate rather than spreading out uniformly over the whole area. To overcome this difficulty it is sometimes necessary to place partitions on the plates which direct the flow of liquid from one downpipe to the other. These partitions often are so arranged that the liquid passes back and forth along the partitions several times before finally reaching the opposite side of the plate to the downpipe. This method of partitioning is of particular advantage in fractionating columns 4 ft. in diameter and greater.

Efficiency of Columns.—Experiments performed at the Massachusetts Institute of Technology have shown conclusively that the efficiency of a fractionating column is not only a function of the intimacy of contact between the liquid and vapor, but it is also a function of other factors, notably the velocity of vapor through the column. In the first place, other conditions being constant, equilibrium between the vapor and the liquid will be more nearly obtained the greater the time of contact between them. This, of course, is obvious, as it merely indicates that the larger the column, the more efficient it becomes. In the same way, the greater the length of time the vapor or the liquid remain in the column, the longer will be their time of contact with each other. In the plate type of column, increased time of contact for the liquid is obtained by increasing the depth of liquid on the plates. This is done by raising the height of the rings and overflow pipes.

Another advantage of the greater depth of liquid on the plates lies in the fact that the bubbles of vapor passing up through the liquid will remain in close contact with it for a greater length of time. It has been shown, however, that when a bubble of vapor emerges from an opening into a liquid, the vapor in the bubble near the surface reaches equilibrium practically instantaneously with the liquid surrounding the bubble, and that the vapor in the interior of the bubble, not being in contact with the liquid, does not come into equilibrium with the liquid except by diffusion of the vapor from the surface of the bubble to the interior and from the interior to the surface. Therefore, if a bubble be introduced into a liquid, it immediately assumes a spherical shape and if allowed to rise through the liquid untouched, practically no further reaction will occur during the greater portion of its travel through the liquid than occurred immediately upon its first contact with the liquid, since the rate of diffusion of the vapor in the inside of the bubble is very slow. In other words, in a plate type column, depth of liquid above a certain amount has no particular advantage insofar as increased time of contact of the vapor with the liquid is concerned, if the bubbles are allowed to rise undisturbed from the point of entrance into the liquid to the surface of the liquid. It has been found, however, that if the bubble be deformed in any way during its passage through the liquid that a fresh portion of the vapor is thereby brought into contact with the surface of the bubble and equilibrium of another portion of the contents of the bubble with the liquid is thereby immediately established.

It should be the object of the designers of the plates in a fractionating column to subject the bubble during its passage through the liquid to as much deformation as is possible. This can be accomplished by several means. In the first place, the bubble may be forced very violently through the opening into the liquid. This violent contact of the vapor with the liquid means that the vapor will be deformed by friction during its passage through the liquid and additional contact may be obtained.

Furthermore, if the caps of a cap-type plate are fairly close together, the bubbles passing through the openings or under the edge of one cap will be thrown violently against the bubbles coming from the adjacent cap, and the two bubbles coming into contact with each other will suffer considerable deformation and therefore the contact of liquid and vapor will be increased at this point. Furthermore, violent agitation of the liquid on the plates by the bubbles will cause the liquid to be thrown into the air in the form of drops. These drops coming into contact with the vapor will tend to reach equilibrium with the vapor just as the bubbles in the liquid tend to react.

Maximum Velocity.—These several effects all show the great advantage of having very high velocity of vapor where it comes into contact with the liquid, and tests have shown that the efficiency of a column rises with the velocity of the vapor and its efficiency rise increases until such a point is reached that the liquid is forced off of the plates entirely by the rush of vapor, under which circumstances, the area of contact is decreased and the efficiency drops off. This maximum velocity, however, for cap-type columns is far in excess of any normal operating velocity. Of course, the more rapid the travel of vapor through the column, the shorter the time it is in the column and therefore the time of contact is less and this must be considered in the design of suitable fractionating device.

One method of obtaining high vapor velocities is to diminish the size of openings through which the vapor passes. Another method is to increase the quantity of vapor which passes through the column, but in either case, increase in velocity is at the expense of increased back pressure, according to the general equation, $V^2 = 2gh$. As was previously pointed out, frequently columns must operate under very low back pressure and therefore the velocity of the vapor which it is possible to obtain is necessarily limited. On the other hand, in most distillation work it is possible to utilize almost unlimited pressure to drive the vapor through the column and therefore to obtain very high vapor velocities.

Summing up, for general purposes, the most efficient fractionating column is the one which offers the greatest surface of contact between the liquid and the vapor and which has the highest vapor velocity where the vapor comes into contact with the liquid.

The Condenser.—The vapor leaving the column then passes to the condenser. The condenser has two and possibly three functions: In the first place, it must supply reflux for the column. In the second place, it must condense the distillate which is discharged from the still, and in the third place, it may assist the column in fractionating the vapor.

The function of the usual type of condenser as a fractionating device is a function which should not be allowed to occur, but which, unfortunately, does often occur in many designs of stills.

The contact between liquid and vapor in a condenser is very poor. Most condensers are of tubular design where the cooling medium and the vapor are inside and outside of the tubes respectively, ~~or the~~ reverse. Under these circumstances, the vapor condensing on the cold surface of the tubes runs down the surface of the tubes while the remaining vapor passes in between the surfaces, keeping out of contact with the condensed vapor as much as possible. This means that one necessary feature of an efficient fractionating device is not complied with in the condenser used for this purpose.

In the second place, condensers must condense differentially and the reflux from the top of the condenser is constantly augmented by additional condensed vapor as it passes down through the condenser until the reflux at the bottom is a maximum. This violates the second rule for efficient fractionating devices.

It is, true therefore, theoretically, and it has been found practically, that by far most efficient results are obtained when as much as possible of the fractionation is required to take place in the fractionating column and as little as possible allowed to occur in the condenser. This leaves but two functions for the condenser to perform, that of furnishing the reflux and that of condensing the remaining vapor to form the distillate. There is no reason why one condenser of size sufficient to take care of both of these functions should not be used to complete the still.

Multiple Condensers.—In most cases, however, modern stills are fitted with two condensers operating in series, the one nearest the column known as the dephlegmator which functions as the reflux condenser, and the second one condensing the balance of the vapor for the distillate.

The use of two condensers in this way, no doubt, originated from the old practice of allowing the condenser to assist in the fractionating, and the dephlegmator was then a finishing device for the column as well as a refluxing device. Operators are accustomed to run stills with the two-condenser system and that type is still preferred in many industries, but is gradually being displaced by the single condenser system. It should be remembered that wherever condensation occurs, enrichment of the vapor takes place, and therefore the reflux condenser has a definite fractionating action. This is, however, small compared with the total fractionation obtained.

Designers of stills have admitted the fallacy of the double-condenser system by placing what is known as a regulating bottle on the discharge from the second or final condenser. This regulating bottle is a device for returning to the column along with the reflux from the dephlegmator, a portion of the distillate condensed in the final condenser, when insufficient fractionation is being obtained in the column or greater capacity is desired, the effect being an increase of the total amount of reflux and, therefore, the greater the fractionating power of the system. Of course, this at the same time cuts down the rate of discharge of the distillate and the net capacity of the system.

Problems in Condenser Operations.—Condensers operate under many difficulties. Some of the difficulties are similar to the difficulties under which the heating coils in the kettles of the stills operate. They also have difficulties peculiar to themselves.

The cooling medium for condensers is usually water, although in some cases, especially in the case of continuous stills, the incoming cold feed is used as a cooling medium whereby the feed is heated to a temperature approaching its boiling point. Under these circumstances, of course, it is perfectly proper to have two or more condensers in series, since the cooling water in the final condenser and the feed in the preliminary condenser can be kept separate. Cooling water, however, may be and usually is dirty, and the feed in the feed heaters may contain materials which precipitate upon heating so that the heating surfaces become incrusted with scale, dirt, etc., rendering them much less efficient. Consequently, the heating surfaces of such condensers have to be cleaned at intervals and the designer of the still must bear in mind this contingency.

Air in Condensers.—Furthermore, most condensers on stills operating at atmospheric pressure, discharge into the open air, so that the air is present in the condenser to a greater or less extent, as will be shown later in discussing the design of heating surfaces. The presence of air with the vapor diminishes the efficiency of the condenser to a very great extent.

Condensers are frequently called upon to serve as coolers, and in the case of very volatile liquids such as ether, methyl alcohol and acetone, where it is necessary to produce a cold distillate, condensers working as coolers must cool the distillate down to very nearly cooling water temperature. Sometimes it is necessary to use brine in addition to cooling water in a separate condenser or cooler, where the temperature of the cooling water is not low enough to cool the liquid satisfactorily, as is often the case during the summer in relatively warm countries.

CHAPTER XII

THE DESIGN OF A DISCONTINUOUS STILL

The previous chapter has described in a general way, the essential features of the discontinuous fractionating still. An example of the design of such a still will now be taken up to show in more detail just how the essential points are taken care of in this connection.

Separation of "Light Oil."—It is required to design a discontinuous still to separate light oil into its relatively pure constituents. Light oil is the more volatile fraction from coal tar in the destructive distillation of coal and consists essentially of benzene, C_6H_6, toluene, $C_6H_5CH_3$, and xylene, $C_6H_4(CH_3)_2$, numerous impurities such as other types of hydrocarbons and carbon bisulphide (CS_2) in greater or less proportion.

Capacity.—The still is expected to handle 1,000 gal. per day of this material. The light oil may be considered to contain 1 per cent of carbon bisulphide, 75 per cent benzene, 10 per cent toluene, 10 per cent xylene and the balance, hydrocarbons of higher boiling point than xylene. Since the still must handle 1,000 gal. per 24-hr. day, enough time must be allowed during the 24 hr. to fill the kettle with the charge, heat the charge up to the boiling point, boil off the respective fractions, dump the residue from the kettle and clean the kettle out, if necessary, in preparation for the next charge. It is customary in large scale discontinuous distillation to handle two days' output as one charge as this means considerably less labor and time lost in filling and emptying and heating up. The kettle, then, must have a working capacity of twice 1,000 or 2,000 gal. of light oil.

Size of Kettle.—Light oil is a liquid which does not foam appreciably when boiling so the disengaging space for vapor in the kettle need not be unusually great. Under these circumstances, it would be good practice to construct the kettle of such size that 2,000 gal. would fill it two-thirds full. In other words, the gross capacity of the kettle would be 3,000 gal. Such a kettle must have a contents of 400 cu. ft. A suitable size would therefore be a horizontal cylindrical, 6 ft. in diameter and 14 ft. long. These dimensions would be modified to a greater or less extent since cylindrical steel kettles of this type come in standard sizes, and dimensions will be selected to conform to such standards.

Heating Surface in Kettle.—The next thing to estimate would be the heating surface required in this kettle which would be in this case in the form of a coil, using high-pressure steam as a heating medium.

The boiling point of benzene is approximately 80°C., that of toluene 111°, xylene (a mixture of three, ortho, meta and para xylene) boils between 138° and 143°C., while the higher boiling residue in the light oil might run as high as 160°C. It will therefore be necessary to use steam of a pressure high enough so that the highest boiling fraction, that is, the residue, can be boiled. One hundred and sixty degrees Centigrade or 320°F. corresponds to 89.7 lb. per square inch absolute steam pressure or 75 lb. gage pressure. The coil, then, should be designed to work, including a factor of safety, at 100 lb. steam pressure and it probably would be found necessary to run the gage pressure on the coils up as high as 80 lb. before distillation was completed.

Methods of Operation.—The distillation may be carried out in several ways, since there are several points of control in a discontinuous system. First, the steam pressure may be controlled; second, the amount of cooling water to the condensers may be controlled; third, the amount of reflux from the condenser to the column may be controlled, or any combination of the three.

In designing a still, therefore, it is essential that certain definite operative conditions be pre-supposed and the design based upon these, and later, if modifications as to design are advisable, it is possible to make changes necessary.

Good practice in distillation work of this sort keeps the flow of water through the condenser constant and controls the steam pressure and the amount of reflux from the condenser to the column. The 1,000-gal. charge should be so arranged that it can be introduced into the kettle in a time not over one hour. It ought to be possible to discharge the residue from a kettle in ½ hr.

Cleaning Kettle.—Light oil, which has been subjected to a preliminary distillation to separate it from the tar contains small amounts of tar which have been carried over as entrainment and, therefore, there will be a certain deposition of tar on the heating coils in the kettle, together with other material which may separate out. This coating of the coils is, however, not excessive in this case and it should not be necessary to clean out the kettle more than once a month, say every 20 days. Since the washout operation would consume a day, 5 per cent of the operative time must be written off for this purpose, or approximately 1 hr. per day charged up for cleaning. The total time, therefore, for filling, dumping and cleaning, 2½ hr. per day must be subtracted from the 24 hr., leaving 21½ hr. available for heating up the charge and distilling it, or, on the 2-day basis, 43 hr. out of 48.

Rate of Heating of Charge.—The rate at which the contents of the kettle will be heated will depend upon the size of coil and the steam pressure within the coil, and since the size of coil is principally a function of the rate of distillation, it is customary to calculate approximately the size of coil needed, assuming a given time required for heating up the charge, and from these first approximations, calculate the time of heating and the actual coil to be provided. It should be possible to heat such a charge to the boiling point in 3 hr., leaving 40 hr. during which the actual distillation must take place.

Method of Distillation.—The method of distillation is as follows: First, cooling water is turned on the condenser so that it is certain that the condenser is operating at its lowest possible temperature. The liquid in the kettle which is now heated to the boiling point sends vapors up through the column which is dry and cold. The cold column will, of course, condense these vapors and the liquid will gradually fill the plates.

Carbon Bisulfide Fraction.—The first fraction which comes over is the carbon bisulphide fraction. Carbon bisulphide boils at 46°C., and in the light oil which has been assumed for this calculation, there are about 20 gal. of this very volatile material. The benzene fraction, which is the one following the carbon bisulphide, should be separated, if possible, entirely from the carbon bisulphide; in other words, it would be desirable to have all of the carbon bisulphide distilled over and withdrawn from the system before any of the benzene is allowed to come over. This means that there must be a very perfect separation or cut between the carbon bisulphide and the benzene fractions. As has been pointed out previously, to obtain a perfect separation is impossible and to obtain anywhere near a perfect separation would require a fractionating device of absurdly large size if the fractionation is carried on automatically, but it is possible by means of reflux control to obtain substantially a sharp cut between the two fractions with a fractionating apparatus of moderate size. The method by which this is done is as follows:

Total Reflux.—The vapor passing up through the column and collecting there is at first mostly carbon bisulphide, but containing a certain amount of benzene, depending upon the degree of fractionation obtained. Suppose, now, the reflux control at the condenser is so arranged that no distillate is taken from the system and all of the vapor which comes to the condenser is returned as reflux to the column. Since the vapor leaving the top of the column and going to the condenser is richer in the more volatile component than the liquid at the top of the column, the reflux which is returned to the top of the column will be, therefore, richer in the more volatile component than the liquid with which it mixes, thereby increasing the proportion of volatile component on the top plate. Continuing, as the composition of the liquid on the top plate increases in the more volatile component, the effect will be felt on the plate below, and after the distillate from the condenser has been returned to the column for a considerable length of time, the effect will be that all of the plates in the upper portion of the column will contain substantially nothing but the more volatile component. When this condition has been reached, if the valve leading from the condenser to the receiver for distillate is then opened, the first portion of vapor which comes over will be that liquid which has collected on the plates in the upper portion of the column and will, therefore, be practically pure component.

When the contents of the column have distilled over in this manner, there will be a sudden break in the composition of the distillate and when this break occurs, the fraction is shifted and a small intermediate fraction is then recovered in a separate distillate receiving tank. If this method of complete reflux of the distillate were not practiced, the amount of intermediate fraction between any two pure fractions would be very greatly increased. In the same way, when the benzene has been nearly all distilled over, it is possible to obtain a sharp cut between the benzene and the toluene fractions by refluxing completely for a certain length of time. There will be, of course, a small intermediate fraction consisting of a mixture of benzene and toluene and this intermediate fraction must be returned and mixed with the next charge which is put into the kettle and redistilled.

The net capacity of any discontinuous still depends to a great extent on the percentage of the liquid distilled which must be taken off as intermediate fractions, since the greater the intermediate fractions, the greater amount returned to the still for redistillation, and therefore the less the net capacity of the still.

In the problem at hand, net 2,000 gal. of light oil must be handled in 43 hr. If an average rate of distillation of 40 gal. per hour be maintained, it is possible to make a preliminary calculation as to the amount of heat which must be introduced into the kettle per unit time. Such a preliminary estimate must then be modified later after the general details and sizes of the equipment have been estimated. The amount of heat which must be put into the boiling liquid depends not only on the quantity of distillate which is to be removed from the still per unit time, but also on the amount of liquid which is returned as reflux from the condenser to the column. It is good practice in discontinuous stills of the type used for fractionating light oil to return as reflux to the column, approximately two times as much liquid as is withdrawn from the condenser as distillate. This reflux is spoken of, therefore, as two to one and for a preliminary estimate of the size of heating coil, this is a satisfactory proportion to assume. It must be realized, of course, that the proportion of reflux to distillate will affect the degree of fractionation which is obtained in the fractionating column, and the fractionating column must, therefore, be based on this ratio.

Operation Cycle.—A suitable cycle, therefore, for the 43 hr. may be as follows:

Character of distillate	Quantity of distillate, gallons	Ratio of reflux to distillate	Time for fraction, minutes
CS_2 Heads	15	2 – 1	25
All liquor from condenser returned to column			10
CS_2 Heads	5	2 – 1	10
Intermediate fraction consisting of CS_2 and Benzene	10	2 – 1	15
Pure Benzene	1,000	1 – 1	1,000
Pure Benzene	450	2 – 1	675
All liquor from condenser returned to column			15
Pure Benzene	5	2 – 1	10
Intermediate Fraction-Benzene and Toluene	60	2 – 1	90
Pure Toluene	150	2 – 1	220
All liquor from condenser returned to column			15
Pure Toluene	5	2 – 1	10
Intermediate Fraction-Toluene and Xylenes	40	2 – 1	60
Pure Xylenes	150	2 – 1	220

It will be noted that there have been withdrawn as separate fractions, three intermediate fractions, one of 10, one of 60 and one of 40 gal., total 110 gal. This intermediate fraction must be introduced into the next charge to be redistilled, which would take approximately 170 min., which, therefore, must be added to the time per cycle, making a total of 2,545 min., or approximately 43 hr. It will also be noted that in taking off the large pure benzene fraction of 1,000 gal., the reflux is indicated as 1 to 1. It will be found in actual practice that when the liquid to be distilled consists largely of one component, as is true in this case, while the first portion of that component is being withdrawn, less fractionation is required than at other periods during the run. Therefore, it is possible to reduce the quantity of reflux needed from say 2 *to* 1 to 1 *to* 1 for a certain period until the next higher boiling component starts to appear in the distillate, when the reflux must be increased again to hold this high boiling component back. This means that for a constant heat input into the system, the rate at which the distillate is recovered will be increased in the proportion of 1½ to 1.

It will be noted that the maximum rate at which a distillate is removed from the system occurs when 450 gal. of benzene are removed in 675 min., with a 2 to 1 reflux. Therefore, the equivalent of three times 450 or 1,350 gal. must be distilled out of the kettle in 675 min., which corresponds to 120 gal. per hour. The latent heat of vaporization of benzene is approximately 167 B.t.u. per pound at the boiling point, 80°C. To vaporize this quantity of benzene per hour, then, would require 167 (B.t.u.) × 120 (gal.) × 8.3 (pounds of water per gallon) × 0.8 (specific gravity of benzene) = 134,000 B.t.u. per hour required. To this must be added heat losses by radiation from the kettle and column.

Lagging.—High temperature distilling equipment of this sort should always be well lagged with suitable heat insulating material such as magnesia or diatomaceous earth, since the heat losses from a bare kettle and column, working at high temperatures are very great. With the apparatus suitably lagged it is safe to assume a heat loss of not over 10 per cent of the heat required for vaporization, making the total heat required per hour 147,000 B.t.u.

Rate of Flow of Heat.—This heat must be introduced into the liquid in the kettle from a steam coil. The amount of coil required is a function of three things: The amount of heat required per unit time, the coefficient of heat transmission from the steam to the liquid, through the coil, and the temperature difference between the steam and the boiling liquid. The amount of heat has already been determined. The coefficient of heat transmission, which is ordinarily stated as B.t.u. (1 B.t.u. is the amount of heat required to raise 1 lb. of water 1°F. in temperature) per square foot of heating surface per degree Fahrenheit temperature difference, must be determined by experiment. A very convenient table, suitable for this case is to be found in "Traite De La Fabrication Du Sucre" by J. de Grobert *et al.*, Self Edition, Technique, Paris, 1913, which is reproduced below.

THE EFFECT OF THE LENGTH AND DIAMETER OF STEAM COILS ON THE COEFFICIENT OF HEAT TRANSMISSION IN BOILING WATER

Copper tube 150 mm. inside diameter; metal 3 mm. thick

Length of coil, meters	Surface of coil in square meters	Kilograms water evaporated per hour per degree Centigrade temperature difference	Pounds water per square foot	Coefficient of heat transmission B.t.u. per square foot per degree Fahrenheit, per hour
2	0.98	3.96	0.83	448
3	1.47	4.84	0.675	364
4	1.96	5.60	0.585	315
5	2.46	6.26	0.522	281
6	2.94	6.85	0.468	252
7	3.43	7.40	0.442	238
8	3.92	7.90	0.413	223
9	4.41	8.43	0.392	211
10	4.90	8.85	0.370	197
15	7.38	10.86	0.302	163
20	9.80	12.52	0.252	136

Copper tube 2 m. long; metal 3 mm. thick

Inside diameter, millimeters	Surface of coil in square meters	Kilograms water evaporated per hour per degree Centigrade temperature difference	Pounds water per square foot	Coefficient heat transmission B.t.u. per square foot per degree Fahrenheit, per hour
10	0.08	1.12	2.89	1,550
20	0.14	1.48	2.17	1,170
30	0.21	1.83	1.79	965
40	0.27	2.07	1.57	846
50	0.34	2.32	1.40	755
60	0.40	2.52	1.29	695
70	0.46	2.71	1.21	651
80	0.53	2.91	1.13	608
90	0.59	3.07	1.07	576
100	0.65	3.20	1.01	544
125	0.82	3.60	0.90	485
150	0.98	3.96	0.83	448

It will be noted from these tables that the coefficient of heat transmission for a given diameter tube is less the greater the length of the tube. This will be readily understood when it is realized that when heating with steam, the steam condenses inside of the tube as water, and as the steam passes through the tube, the quantity of water mixed with the steam becomes greater and greater. Water is a good insulator of heat and therefore the greater the quantity of water present in the coil, the lower the coefficient of heat transmission from the steam through the water and coil to the boiling liquid outside. Other things being equal, then, heating coils should be made as short as possible. Their length is usually, however, limited by questions of construction and design.

It will also be noted that for tubes of a given length, the coefficient of heat transmission decreases as the diameter of the tube increases. This may be explained by the fact that the ratio of circumference to area of a small circle is greater than that for a large circle, and for a given volume of steam passing through a tube, the contact of the steam with the surface of the tube is greater the smaller the tube. The steam sweeping through the tube tends to sweep along with it by friction, the water which is condensed out on the surface of the tube, and, therefore, the greater the frictional effect, the less will be the thickness of the insulating water layer between the steam and the metal. It is evident, again, that while the small tube is more efficient than the large tube, the actual choice of tube to be used in any given case is frequently determined by questions of design and construction.

Size of Coil in Kettle.—For a kettle of the size needed for the still in question, a copper steam coil approximately 2 in. inside diameter would be a suitable size, and the minimum length which would be possible in a kettle 14 ft. long would be one tube running approximately the full length of the kettle, or, say, a tube 12 ft. long. Based on the data given in the table, the coefficient of heat transmission for a 2-in. tube, 12 ft. long would be approximately 558 B.t.u. per square foot of heating surface per degree Fahrenheit temperature difference.

Temperature Difference.—The third factor affecting the amount of heating surface in the kettle is the temperature difference between the steam and the boiling liquid. Benzene boils at 80°C. while the higher boiling hydrocarbons remaining in the kettle while the xylene fraction is being removed, have a boiling point of perhaps 160°C. It would be good practice in operating a still handling this material to increase the steam pressure and therefore the steam temperature as the temperature of the boiling liquid increased, keeping the temperature difference between the steam and the boiling liquid approximately constant. This method of operation was assumed in the cycle of distillation noted above, indicating a constant rate of heat input into the kettle and, therefore, a constant rate of distillation. It is good practice under these circumstances to keep a temperature difference of approximately 40°F. During the period when the benzene fraction is being removed, the temperature of the liquid in the kettle will be substantially that of boiling toluene or 110°C. This corresponds to 252°F. or 16 lb. gage steam pressure. The heating surface required in the coil, therefore, would be

$$\frac{147{,}000}{558 \times 40} \text{ or } 6.62 \text{ sq. ft.}$$

The 2-in. tube has approximately 0.5 sq. ft. of heating surface per linear foot of length. Therefore, a coil a little over 13 ft. long would be indicated. It is customary in designing these heating surfaces for distilling and evaporating equipment, to increase the calculated heating surface by a certain percentage known as the factor of safety and it is good practice in a discontinuous still to use a factor of safety of 50 per cent, giving a heating surface of 10 sq. ft. In this particular case, however, the light oil will contain a certain amount of tarry material which will eventually tend to incrust the heating surface and render it less efficient. It would be better, therefore, in this case to use a greater factor of safety than is ordinarily used.

It was specified that the coil would have tubes approximately 12 ft. long. Twenty square feet would require a tube 20 ft. long. Under the circumstances, the coil would probably be made up of 2 to 12-ft. lengths, running side by side through the kettle, the coils being parallel, steam inlet to the coil dividing inside of the kettle, and the two coils joining together at the farther end for the exhaust. It might also be possible to make these two coils as one coil with a return bend at the further end of the kettle, making the coil, therefore, one tube, 24 ft. long. This would cut the coefficient of heat transmission down from approximately 558 to 350 and the factor of safety would, therefore, be reduced in proportion.

Accessories.—The accessories to be used in connection with the heating coils would be a throttle valve to control the steam pressure, a pressure gage to record the steam pressure and a trap on the exhaust end to remove the condensed steam as rapidly as it accumulates. The coils should be given a slight slope toward the exhaust to insure proper drainage of the condensed steam.

CHAPTER XIII

THE FRACTIONATING COLUMN

Experience has indicated that the most efficient type of fractionating column when back pressure is not of great importance, is the plate column. Where back pressure must be kept down, the filled type, with filling of some suitable material is necessary. The plate type column, fitted with boiling caps, has come to be recognized as best suited for difficult separations as the separation of Benzene and Toluene. The design of such a column is the chief factor in the success or failure of the whole still as a fractionating device. The information on which such a design is made is a mixture of scientific and empirical data and the design must depend on past good practice to a great extent, owing to the lack of carefully made experiments on this subject. A certain amount of information is available in the works of certain French authorities such as Barbet, Savalle, Sorel, and Mariller, where the relative efficiency of certain types of boiling caps in plate columns is given. These data are, however, of little value, since as has been pointed out, the fractionation obtained in a column is a direct function of the ratio of reflux to distillate, and these data are quite lacking in this respect. Any comparison of the fractionating efficiencies of different types of plates and boiling caps must take into consideration the ratio of reflux to distillate as well as the increase of concentration from one plate to the next above.

Size of Boiling Cap.—It has been pointed out that for given conditions, the cap which brings the vapor into most intimate contact with the liquid, will prove to give the most efficient fractionation. The slotted cap has been found to be most satisfactory in this respect, and this type will be discussed with reference to the present design. Since the ratio of the circumference of a circle to the area increases as the diameter decreases, the smaller the cap, the more surface of contact between liquid and vapor. But manufacturing considerations limit the decrease in size below a certain diameter. For most work, a cap 4 in. in diameter is a minimum. The slots in the sides of the cap should be as narrow and as close together as possible. Since, however, the constant rush of wet vapor through these slots, and often the presence of more or less corrosive liquids, gradually wears away the metal, there must be enough width of metal between the slots to give the caps a reasonable life.

Pressure Drop in Column.—The height of the caps and the distances between them depend on the depth of liquid on the plates and the velocity of vapor through the column. The difference in pressure between any two plates of a column is a function of three things, the depth of liquid on the plate, the velocity of vapor through the slots of the cap, and the friction of the vapor passing through the slots and liquid. The total pressure, E_p, is therefore the sum of the pressure due to the static head of liquid (h_e) above the center of pressure on the opening of the slot, plus the velocity head which can be calculated from the expression:

$$V \text{ (velocity)} = \sqrt{2gh}$$

(where g is the acceleration due to gravity and h is the velocity head), plus the pressure loss due to friction. The usual velocities obtained in distilling columns are in the vicinity of 10 ft. per second. Experiments have shown that the friction of vapors through orifices when the velocities are less than 100 ft. per second, is very small, and under this velocity of 10 ft. per second, can be neglected. Therefore,

$$E_p = h_e + \frac{cV^2}{2g} \text{ approximately}$$

where c is some constant to be determined by experiment. The author has obtained values of c from 2.8 to 2.0 for varying types of slotted caps; 2.4 is a fair average. It should be remembered that the static head h_e is not the total depth of liquid on the plate, but the distance from the surface of the liquid to the center of pressure on the opening of the slot. Furthermore, the amount of opening in the slot is a function of the volume of vapor passing through it, the greater the volume of vapor, the lower the liquid level inside of the cap, and the greater the slot opening. Therefore, the static head is also a function of the velocity of vapor through the column. This head may be estimated as consisting of two portions, the static head above the top of the slot (h_1) and the head opposite the slot itself, which is approximately two-thirds of the slot opening (l) or

$$h_e = h_1 + \frac{2}{3} l$$

It is possible to calculate the slot opening (l) if the volume of vapor that passes through it per unit time is known, from the gas law PV = NRT and the width of the slot. Slots should be so designed that when operating at full capacity, they will be wide open. The vapor passing through the slot is subject to several effects. It has a horizontal velocity, V, due to its passage through the slot. It also has a vertical velocity component V_1 due to its being lighter than the liquid. Its travel is also influenced by the friction of the surrounding liquid. The net result of these several forces is that the horizontal motion through the slot is changed immediately to one in an upward direction, and the bubble, if unobstructed, assumes a parabolic path, and after a short travel rises vertically through the liquid to the surface.

Contact Between Vapor and Liquid.—The object of the designer of the plate is not only to bring finely divided bubbles into contact with the liquid, but also to deform them as much as possible during their passage through the liquid in order to bring fresh interior vapor to the surface of the bubble. The caps, therefore, should be placed closely enough together so that the bubbles from one cap come violently in contact with those from the adjacent cap before they have had an opportunity for assuming a vertical direction. In fact, the contact of the bubbles should occur while they have still retained a nearly horizontal motion, thus insuring no dead space between the lower portions of the caps where the liquid can pass along without having bubbles coming into contact with it. For the same reason the slots should come as near to the bottom of the liquid as possible, and should be designed to operate at full opening under normal load.

Overflow Pipe.—The depth of liquid on the plate is regulated by the height of the overflow pipe, which is usually a vertical cylindrical pipe open at the top horizontally. The liquid must, therefore, rise above the edge of the pipe in order to overflow into it, and this additional height can be estimated by means of the weir formula

$$Q = 3.33lh^{3/2}$$

where Q is the volume of liquid passing through the pipe in cubic feet per second, l is the circumference of the pipe in feet, and h is the height of the liquid above the edge of the pipe in feet. Practically, due to the violent agitation on the plate a large amount of liquor splashes over the edge of the downpipe, but the discharge is approximated by the above method. The level of liquid on the plate should be but a short distance above the top of the slots in the caps, since there is but little advantage in having the bubbles rise vertically through a great depth of liquid. Under some circumstances, however, it is desired to make the time of passage of the liquid down through the column considerably longer than usual, for instance in the exhausting columns of continuous stills where all the more volatile component must be removed from the liquid. This is most conveniently done by increasing the depth of liquid on the plates.

Distance Between Plates.—The distance from one plate to the next above depends upon the depth of liquid on the plate, the character and spacing of the caps, and the velocity of the vapor. The bubbles bursting at the surface of the liquid throw off a fine spray of liquid. In addition to this bubble spray, two or more bubbles coming to the surface together carry in between them a solid mass of liquid which is thrown into the vapor space when they burst. The greater the velocity and the greater the number of the bubbles, the greater this entrainment. One serious cause of the inefficiency of the plate column is this entrainment, which carries the liquid from one plate to that above. Therefore, the plates should be far enough apart so that most of the liquid spray has an opportunity to settle before it is carried into the caps above. This distance should never be less than 6 in. above the liquid level, for ordinary vapor velocities.

Number of Plates.—The number of plates needed for the fractionating column depends upon the several factors noted previously; namely, first, the degree of separation of the components desired; second, the relative ease of this separation; third, the ratio of reflux to distillate; and fourth, the efficiency of the plates. The degree of separation is determined by the problem and usually means practically complete separation of the respective components. The ease of the separation can be determined from the boiling point curves described previously, the number of steps in passing from the quality of residue desired to that of distillate desired determining the number of theoretically perfect plates to be used. For instance, to produce practically pure benzene, leaving practically pure toluene behind would take approximately 15 steps. Since, however, a perfect column would have infinitely great reflux, the plates are not perfect, and for the usual reflux of 2 to 1, the efficiency averages 33 per cent. The actual column would then require 15 ÷ .33 = 45 plates. For a more accurate determination, the method used in Chapter X should be used. A 45-plate column would, however, be excessively high for practical purposes, so under the circumstances, a shorter column would be used, say 36 plates. The effect of this shorter column would be to prohibit sharp cuts at the ends of the various fractions, and this difficulty is then overcome by the system of total refluxing described above, when no distillate is drawn off, and the entire energy of the still is devoted to separating the components in the column.

Diameter of Column.—Suppose for the present case boiling caps are selected such that the slot area per cap is 4 sq. in. for a cap 4 in. in diameter, and suppose that it has been found by experiment that the caps should be about 2 in. apart, it is then possible to estimate the number of caps per plate and the approximate diameter of the column.

It was estimated that approximately 147,000 B.t.u. would be needed per hour to operate the still in question. This corresponds to

$$\frac{147,000}{167} = 880 \text{ lb. of Benzene per hour}$$

passing as vapor through the column. The molecular weight of Benzene (C_6H_6) vapor is 78. Therefore, 78 lb. of the vapor occupy 359 cu. ft. at standard conditions, 0°C. and 1 atmosphere pressure. Since the pressure in the column is substantially atmospheric, the temperature of the vapor will be that of the boiling point of Benzene at atmospheric pressure, 80°C. The volume of vapor passing through the column per hour will be

$$\frac{880 \times 359 \times 353}{78 \times 273} = 5{,}240 \text{ cu. ft. and}$$

$$\frac{5{,}240}{3{,}600} = 1.46 \text{ cu. ft. per second.}$$

Since the velocity of the vapor through the slots in the caps has been taken at 10 ft. per second, the slot area per plate would be

$$\frac{1.46}{10} = 0.146 \text{ sq. ft.} = 21 \text{ sq. in.}$$

Allowing a slot area per cap of 4 sq. in., five caps would be required per plate, and with a minimum distance between caps of 2 in. the plate layout would be as follows:

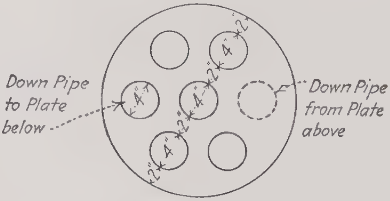


FIG. 27.—Arrangement of caps on plate.

This would make the diameter of the plate and therefore of the inside of the column, 20 in.

Height of Column.—The height of the column is calculated from the number of plates, 36, times the height of each section, which is 2 in. of liquid plus 6 in. of vapor space.

$$36 \times \frac{2 + 6}{12} = 24 \text{ ft. high}$$

Vapor Pipes.—The vapor connections from the kettle to the column and from the column to the condenser should have a vapor velocity of not over 50 ft. per second. The diameter would be

$$\frac{1.46}{50} = 0.029 \text{ sq. ft.} = 4.2 \text{ sq. in.}$$

A 3-in. diameter vapor connection would be used.

CHAPTER XIV

THE CONDENSER

The condenser receives all of the vapor leaving the top of the fractionating column. Some of the factors influencing the design of the condenser have been discussed previously. The decision as to the number of condensers to be used often depends upon circumstances. It is felt that except under unusual conditions a single condenser, large enough to take care of all of the reflux and condensation required is the most economical design for a discontinuous fractionating still. It is usually customary to cool the condensed distillate below its boiling temperature since a hot distillate is readily volatilized and is therefore likely to suffer loss by evaporation on standing and, furthermore, in case the vapor is inflammable, a hot distillate is a considerable source of fire risk. In small distilling apparatus it is customary to make the condenser large enough to furnish the necessary cooling. It is sometimes simpler, however, to furnish a supplementary cooler to receive the distillate from the condenser.

Factors Influencing Condenser Design.—The various factors which influence the design of the condensing system are as follows:

1. The amount of heat which must be removed by the condenser in condensing the vapor.
2. The amount of heat which must be removed by the condenser in cooling the condensed vapor.
3. The amount of vapor entering the condenser from the fractionating column.
4. The amount of inert gas or other non-condensable vapors present in the vapor entering the condenser.
5. The temperature of the vapor entering the condenser.
6. The temperature of the non-condensable gases leaving the condenser.
7. The temperature of the condensed vapor leaving the condenser.
8. The amount of cooling liquid available.
9. The temperature of cooling liquid available.
10. Temperature at which cooling liquid should leave the condensing system.

11. The velocity of vapor by the cooling surface.
12. The velocity of the cooling liquid by the cooling surface.
13. The removal of non-condensable gases from condenser.
14. The physical characteristics of the condensed vapor.
15. The physical characteristics of the cooling liquid.

It will be advisable to discuss these various factors and their influence on the design of condensers in connection with the present design for the distillation of light oil.

Heat Removed in Condenser.—The first factor, the amount of heat to be removed by the condenser in condensing the vapor is obviously the latent heat of vaporization of the liquid which is condensed. It will be recalled that the coil designed for the kettle in this distilling equipment was to furnish 147,000 B.t.u. per hour. This quantity of heat, however, included a 10 per cent allowance for heat losses by radiation from the kettle and column and therefore the actual heat of vaporization to be removed from the condenser would not include this additional 10 per cent and would therefore amount to 134,000 B.t.u. per hour.

Heat Removed in Cooling Distillate.—The second factor, the amount of heat to be removed in cooling the condensed vapor depends upon the temperature to which this condensate is to be cooled, which we may assume in this case to be 30°C. or 86°F., 90°F. below the condensing temperature of the benzol vapor. The amount of heat which must be removed in order to cool this distillate, then, will be the drop in temperature times the weight of the distillate times its specific heat. The specific heat of benzol may be taken to be approximately 0.45 and the weight of benzol condensed per hour is approximately 800 lb., making the amount of heat which must be removed by cooling approximately 32,000 B.t.u. per hour.

Non-condensable Gases.—The fourth factor, the amount of non-condensable gases in the vapor is a factor of extreme importance. This will be realized when it is stated that the coefficient of heat transfer from a condensing vapor to a solid wall is ordinarily considered to be in the vicinity of 2,000 B.t.u. per square foot of condensing surface per degree Fahrenheit temperature difference per hour, while the coefficient of heat transmission between a gas and a cooling wall is usually not greater than 10 B.t.u., this value, however, depending upon the velocity of the gas by the cooling surface. It is obvious, then, if there is any appreciable amount of vapor or non-condensable gas present in the condensing vapor that the coefficient of heat transmission between it and the condensing surface will be decreased enormously since the non-condensable gas has the unfortunate property of attaching itself fairly firmly to the condensing surface and furnishing an excellent insulating layer between it and the vapor.

In the particular problem in question, however, the fractional distillation of light oil, after the head products, that is, the carbon bisulphide, etc. have been removed, there is present in the vapor passing to the condensers comparatively little inert gas and therefore it may be assumed that the amount of non-condensable gases in the vapor during the greater part of the distillation is very small. These gases must be provided for, however, and it is customary to arrange the outlet from the condenser in such a way that the gases may pass to a subsequent cooler or scrubber where any valuable vapors contained in them may be recovered.

Vapor Temperature.—The fifth factor involved is the temperature of the vapor entering the condenser, which during the period when benzol is being distilled off will be approximately 80°C. or 176°F.

Exit Gas Temperature.—The sixth factor, the temperature of the gases leaving the condenser, depends to a certain extent on the design of the apparatus. It has been found in practice that the condensed vapor, depositing on the cooling surface tends to cling to that surface while the balance of the vapor tends to pass down through the center of the tube in case the vapor is passing through the tubes of the cooler, or in the case where the vapor is passing around the tubes, the vapor tends to pass between them and not come into direct contact with them. Consequently, the liquid reaching the bottom of the condenser, having been in contact with the cold walls of the condenser will be at a temperature lower than that of the vapor in between the tubes and it has been found that the gases finally leaving the condenser may have a temperature perhaps half way between the condensing temperature of the bulk of the vapor and the temperature of the cold liquid at the bottom.

The seventh factor, the temperature of the liquid leaving the condenser, has been discussed above.

Cooling Water.—The eighth factor, the amount of cooling liquor available, is, of course, dependent upon local conditions. Where water is the condensing and cooling liquid, it is often present in substantially unlimited quantities, and, therefore, it is customary to assume a reasonable temperature rise of the cooling water, in this case amounting perhaps to within 20°C. or 38°F. of the temperature of the condensed vapor.

The ninth factor, the temperature of the cooling water, if assumed to be 20°C. or 68°F., it will enable the total quantity of water to be used to be estimated as noted below.

The tenth factor, the temperature at which the cooling liquid should leave the condenser, is sometimes of importance if this liquid is to be used for other purposes. It is frequently true that in chemical plants, materials of varying volatility are handled and cooling water which would be too warm to condense satisfactorily a volatile material, might be perfectly satisfactory for condensing vapors with a higher boiling point, and, therefore, in cases of this sort, it is sometimes possible to use moderately warm cooling water discharged from the condenser of one distilling equipment for cooling the condensers in the apparatus handling the liquid of the high boiling point. If this is true, then, the maximum temperature rise which could be permitted for the cooling liquid would be limited.

Vapor Velocity.—The eleventh factor, the velocity of the vapor by the cooling surface, is of importance from two standpoints: In the first place, when vapor condenses on a cooling surface, it tends to adhere to that surface and furnish an insulating layer of liquid between the balance of the vapor and the cold walls. If the vapor be hurled past this surface at high velocity, the film of liquid will be swept off of the cold surface by friction and its thickness will be reduced, therefore enabling the following vapor to come into closer contact with the walls.

In the second place, if there are non-condensable gases present in the vapor, these gases, if allowed to adhere to the condensing surface, will decrease the cooling efficiency of such surfaces to a very great extent and a high vapor velocity past these surfaces will tend to remove this gas or prevent its adhering to the walls, therefore increasing the coefficient of heat transmission to a marked extent.

The necessity of high velocity for vapors has been known for many years in such industries as the evaporator industry where special provisions are always made in the heating surfaces of multiple effect evaporators to remove these non-condensable gases as rapidly and as thoroughly as possible.

Cooling Water Velocity.—The importance of the twelfth factor, the velocity of the cooling liquid by the cooling surface is not sufficiently realized by most people. The rate of flow of heat from a condensing vapor to the cooling wall, through the cooling wall and to the cooling liquid is proportional to the coefficient of heat transmission and the temperature difference per unit area. The coefficient of heat transmission, K, is made up, in this case, of three coefficients:

First, the coefficient of heat transmission from the vapor to the wall

Second, the coefficient of heat transmission through the wall itself, and

Third, the coefficient of heat transmission from the wall to the cooling water.

Coefficient of Heat Transmission.—If these three coefficients are known, it is possible to calculate the overall coefficient in this fashion. The reciprocal of the coefficient of heat transmission, that is, $\frac{1}{K}$ or the resistance, is equal to the sum of the individual resistances or the sum of the reciprocals of the various values of K; that is,

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}$$

where k_1 is the coefficient of heat transmission between the condensing vapor and the wall. This, for a vapor containing no non-condensable gases would be in the vicinity of 2,000.

The coefficient of heat conductivity of copper is about 220 B.t.u. per square foot of cross-section per degree Fahrenheit temperature difference per hour per foot of thickness. For thin copper tubes, such as those of which such condensers are constructed, with walls 0.06 in. thick, the value of k_2 for the metal would be about 44,000.

Film Coefficient Water Side.—k_3, the coefficient between the wall and the water, is given approximately by the expression $k_3 = 450\ \bar{V}^{3/4}$, where V is the linear velocity of water by the cooling surface in feet per second. To show the effect of the water velocity on the value of k_3, if

$$\begin{aligned}
V &= 0.01 \text{ ft. per sec.}, & k_3 &= 14 \\
V &= 0.1 \text{ ft. per sec.}, & k_3 &= 80 \\
V &= 1.0 \text{ ft. per sec.}, & k_3 &= 450 \\
V &= 10.0 \text{ ft. per sec.}, & k_3 &= 1{,}400
\end{aligned}$$

If, now, the overall coefficient of heat transmission, K, be calculated as above, using for k_1 a value of 1,000 instead of 2,000, since the vapors in question contain small amounts of non-condensable gases, for a linear water velocity of 0.1 ft. per second

$$\frac{1}{K} = \frac{1}{1{,}000} + \frac{1}{44{,}000} + \frac{1}{80} \text{ or } K = 74$$

whereas for a water velocity of 1.0 ft. per second

$$\frac{1}{K} = \frac{1}{1{,}000} + \frac{1}{44{,}000} + \frac{1}{450} \text{ or } K = 313$$

and when the water velocity is 10 ft. per second

$$\frac{1}{K} = \frac{1}{1{,}000} + \frac{1}{44{,}000} + \frac{1}{1{,}400} \text{ or } K = 576.$$

It will be noted that where the water velocity is low, the overall coefficient, K, is low and the film resistance between the wall and the water of 80 is substantially the same as the overall coefficient from vapor to water of 74; in other words, the conductivity of the vapor to wall and of the wall itself will make but very little difference. Where the water velocity is moderate, 1 ft. per second, the film conductivity for water is 450, while the overall coefficient is 313. In this case the film resistance between the vapor and the wall of 1,000 is of importance and where the water velocity is high, it is, therefore, necessary to insure as much freedom from non-condensable gases on the vapor side as possible. Where the water velocity is very high, in the case of 10 ft. per second, the film conductivity for the water being 1,400 and the overall coefficient of conductivity 576, the thickness and material out of which the tube is made, as well as the conductivity on the vapor side, are of importance, and under such circumstances it is advisable to use as thin metal walls as conditions will permit.

Removal of Non-condensable Gases.—The thirteenth factor, the removal of non-condensable gases, must be positive. There must be no pockets or dead spaces in the vapor space of the condenser, to permit these gases to accumulate. There must be a steady flow of vapor through all portions of the condenser, forcing all gases to the vent, which should be arranged in such a way that there is no possibility of its being sealed shut by distillate collecting in the vent pipe.

It is preferable, if possible, to operate the condenser under a pressure slightly greater than that of the atmosphere, so that there will be a positive flow of gases from the condenser into the atmosphere. This has the added advantage that the air under these circumstances cannot work its way back into the condenser and partially insulate the cooling surfaces. If the pressure difference between the inside of the condenser and the atmosphere is great, a certain amount of the condensed vapor will escape through the vent and provision must be made by means of a supplementary cooler, scrubber or condenser to retain this.

Characteristics of Vapor.—The fourteenth factor, the physical characteristics of the condensed vapor, is of importance in two respects:

First, the specific heat of this condensed vapor must be known in order to calculate the cooling, as was done above.

Furthermore, if the condensed vapor has excessive viscosity, which will tend to make it flow slowly over cooling surfaces, this must be allowed for in proportion to these surfaces. In the case of the benzol in question, the viscosity is about the same as that of water and may be neglected.

Characteristics of Cooling Water.—The fifteenth factor, the physical characteristics of the cooling liquid are especially important when the cooling liquid is water and that water comes from a relatively impure source. Many chemical plants are so located that they must use for cooling water, water containing all sorts of sediment, scale-forming materials, etc., and invariably under these conditions, the cooling surface becomes coated with layers of material which usually act as excellent heat insulators. It is, therefore, necessary under these circumstances to design the condenser so that the cooling surfaces on the water side can be readily cleaned. This is usually done by making the water flow through the tubes and in the case of a vertical tubular condenser, it is possible, by removing the top of the condenser to run a swab down through the tubes and clean them out. In the case of certain types of stills where the material which is to be distilled is run through a vapor heater which is part of the condensing system, the material may deposit out scale or dirt on heating in the same way, and similar precautions must be taken.

Logarithmic Mean Temperature Difference.—It has been assumed for the particular design in question that cooling water comes in at 68°F. and goes out at 140°F. and that the total heat to be removed in condensing and cooling the distillate is 166,000 B.t.u. per hour. The proportional rise in temperature of the cooling water for cooling purposes, then, will be 14° out of a total of 72°, or if the cooling takes place entirely after the condensation has occurred, the cooling water will rise from a temperature of 68 to 82°F. and then will rise from 82° to 140° during the condensing period. Since the flow of heat from one fluid to another is proportional not only to the coefficient of heat transmission but to the temperature difference, it is necessary to figure this temperature difference between the vapor and the cooling water and also to figure the temperature difference between the condensed vapor which is being cooled and the cooling water. This is done by use of what is known as the logarithmic mean, and in the case of a counter current condenser and cooler, where the coldest cooling water cools the coldest distillate and the hottest cooling water cools the hottest vapor, the temperature difference for the condensing period would then be calculated as follows:

$$\Delta T = \frac{(176 - 82) - (176 - 140)}{\ln \dfrac{176 - 82}{176 - 140}}$$

where ln is the logarithm to the base e. This is equivalent to 60°F.

For cooling the condensed vapor we also use a logarithmic mean temperature difference which in this case will be

$$\frac{(176 - 82) - (86 - 68)}{\ln \dfrac{176 - 82}{86 - 68}}$$

which equals 46°F.

Surface for Condensing.—The surface required for condensing, then, will be

$$\frac{134{,}000}{313 \times 60} = 7.1 \text{ sq. ft.}$$

It will be noted that the value of coefficient of heat transmission, K, has been used as 313, this assuming a water velocity in the condenser of 1 ft. per second. This is an approximation which may or may not be justified by the results of the calculation as will be noted below. In the same way the coefficient of heat transmission during the cooling period may be figured as follows:

$$\frac{1}{K} = \frac{1}{450} + \frac{1}{44{,}000} + \frac{1}{80}, \quad K = 67.8$$

It will be noted in this case that a value of 450 is selected as before for the coefficient on the cooling water side, assuming a cooling water velocity of 1 ft. per second, while the coefficient on the condensed vapor side has been selected as 80, assuming a velocity of this condensing liquid as of 0.1 ft. per second.

Surface for Cooling.—This coefficient for cooling, then, will be equal to 68 and the surface required for cooling will then be

$$\frac{32{,}000}{68 \times 46} \text{ or } 10.2 \text{ sq. ft.}$$

making a total surface required for the condenser of 17.3 sq. ft. To this must be added a certain amount as factor of safety, due to inexact requirements and the possibility of dirty condenser tubes. Fifty per cent factor of safety would be suitable under these circumstances and if tubes 1¼ in. in diameter were used in the condenser there would be required, therefore, approximately 78 ft. of tubing. If the condenser were built up in the form of a number of straight tubes side by side, the so-called tubular type, and the tubes were 6 ft. long, there would be required 13 such condenser tubes. It is now possible to obtain a more accurate estimate of the cooling water velocity through such a condenser. If the water were to pass through the tubes and the vapor were to be outside the tubes, and the condenser were to be of the one-pass type, that is, water going through the tubes once, the area of 13 tubes would be the area through which the cooling water would flow. This would amount to approximately 0.111

sq. ft. for the 13 tubes. The amount of cooling water per second would be

$$\frac{166{,}000}{72 \times 3{,}600 \times 62.4}$$

or 0.0103 cu. ft. per second, where 166,000 is the heat taken up by the water per hour, 72 its rise in temperature in degrees Fahrenheit, 3,600, number of seconds per hour and 62.4, the weight in cubic feet per hour. This would indicate a velocity through the tubes of 0.1 ft. per second if all the tubes were in parallel; in other words, the coefficient of heat transmission would have been 74 instead of 313 estimated above. In order, therefore, to increase the water velocity to approximately ten times 0.1 ft. per second it will be necessary to send the water through each tube separately; in other words, to have a multi-pass condenser with as many passes as there were tubes; that is, 13. Such condensers would be difficult to build and rather expensive and therefore it would be better practice to use fewer tubes and increase their length, thereby increasing the heating surface and also increasing the water velocity. The designer of condensers, therefore, must balance water velocities against cost of construction, and the type of condenser and size finally selected will, therefore, depend to a very great extent upon the cost of manufacture of the various types which are possible. Yet it is usually found that a single-pass condenser in moderate sizes is less expensive to construct than a multi-pass high speed condenser where the amount of cooling surface, it is true, is considerably less, but where the cost of construction per unit surface is considerably greater.

CHAPTER XV

ACCESSORIES

A fractionating still must have numerous accessories and attachments in order to permit of its accurate control. It is essential in the first place that a constant supply of steam be assured. This can only be accomplished by having a constant steam pressure available at the steam coil. Since in most chemical plants the load on the boiler plant fluctuates, and since the firing of such boiler plants is likely to be irregular, the boiler pressure almost always is variable and this variability will be transmitted to the heating coils of the distilling apparatus unless special precautions are taken. These precautions are usually in the form of constant pressure reducing valves between the boiler and the still, whereby a constant pressure on the steam coils may be assured no matter what variations may occur in the boiler pressure itself.

The condensed steam in the coils of the kettle must be removed as rapidly as it collects; otherwise the water will collect in the tubes, and blanket the surface, causing the rate of evaporation of the still to drop off immediately. This means that there must be efficient steam traps attached to the coils and these traps must be always kept in perfect working condition.

Indicating Valves.—The throttle valve which controls the steam pressure on the coils should preferably be constructed in such a way that the amount of opening of the valve can be registered by means of an indicator on a dial or some device of that type. This enables the still operator to reproduce his valve opening and therefore his still pressure from charge to charge without necessitating the inspection of steam gages, etc. In the same way, the valves which control the flow of cooling water to the condenser should be fitted with indicating devices for the same purpose.

Testers or Weir Boxes.—The rate of flow of the distillate from the condenser to the receiving tank must be measured. This is usually done by means of so-called testers or weir boxes, where the rate of flow is measured by the depth of liquid flowing through a suitable slot or opening. It is also necessary to take samples of distillate from time to time and the piping should be arranged with suitable connections so that this may be done conveniently, since in the fractional distillation of such liquids as light oil it is not possible to rely entirely on temperature readings in order to determine the quality of the distillate obtained, as thermometers do not give the degree of purity in sufficient precision and it is necessary to withdraw samples from time to time and test them in the chemical laboratory in order to determine exactly the degree of purity of the distillate.

Location of Controls.—Finally, for the convenience of the operator and for general efficiency of the distilling apparatus, all control valves should be located at one spot. The operator must not be required to climb three or four stories of the building in order to operate the steam control valves and water control valves and inspect the rate of flow of distillate, but all of these valves, and testers, etc. should be so arranged that the operator, standing in one place, can have the still under complete control.

Special Designs.—It should be pointed out that the preceding discussion of the design of suitable still for the fractional distillation of light oil has been for the purpose of familiarizing the reader with the various factors which are involved in the design of such apparatus and that the particular design evolved is not necessarily the best design for all conditions under which light oil might be distilled. It should be remembered that the design of all chemical engineering machinery depends to a very great extent indeed upon local and special conditions and, therefore, it is not possible for a designer to produce a machine suitable for everybody at every place. This accounts for the fact that most manufacturers rarely carry so-called standard equipment in stock and must, in nearly every case, design special equipment suited for the particular requirements of the problem involved.

CHAPTER XVI

CONTINUOUS DISTILLATION

The previous chapters have taken up in considerable detail the question of intermittent distillation. Continuous distillation differs from intermittent distillation in that the material to be distilled is fed continuously into the machine, the products of the distillation are withdrawn continuously and the state of the components in the mixture being distilled remains a constant at any point in the system. That is, the temperature, pressure and composition of the liquid and vapor at any point in the apparatus remains unchanged so long as external influences are constant.

Requirements for Continuous Distillation.—The requirements for the suitable utilization of continuous distillation are three in number:

First, the feed of material to be distilled must be constant.

Second, the source of heat or other form of energy used in operating the still must be constant.

Third, there must be available constant cooling fluid for condensers, etc.

Constant Rate of Feed.—*Requirement No.* 1, the constant feed, assumes that the rate of flow of feed liquor to the still must be arranged so that it does not change from one time interval to another, and it also assumes that the quality or composition of this liquor remains unchanged. It is therefore obvious that, in general, continuous distillation is suitable especially for the handling of relatively large amounts of a fairly uniform material. Since, also, continuous distillation involves careful regulation of the apparatus at the beginning of the handling of such material and since such regulation is sometimes difficult, it is advisable to use continuous distillation only where large amounts of fairly uniform material are expected over extended periods of time.

Constant Steam Supply.—*Requirement No.* 2, constant source of heat supply for operating the still, is essential so long as the still is to be semi-automatic in operation; that is to say, if steam is to be used for heating there must be some suitable device in connection with the steam lines such that the steam pressure may be automatically kept constant. Usually, the source of steam available for distillation is the steam boiler and since the boiler pressure is a variable quantity, depending upon firing conditions and demands on the boiler from other units, it is essential to use steam pressure sufficiently below that of the boiler pressure available so that suitable reducing valves placed on the line will function properly, giving a reasonably constant steam pressure at the still. Furthermore, most continuous stills are very sensitive to slight changes in steam pressure applied and it is therefore necessary to use in addition to the constant pressure reducing valve mentioned above some sort of sensitive steam regulator which will automatically maintain a constant pressure in the still.

Constant Water Supply.—*Requirement No.* 3, constant supply of cooling fluid, usually water, infers constancy with regard to both amount and temperature, since the quality and amount of distillate obtained is a function of the amount of reflux which depends largely on the dephlegmation obtained in the reflux condenser.

Results of Continuous Distillation.—In general, the results obtained in continuous distillation are:

1. Constant products of distillation.
2. Constant conditions at any point in the system.

So far as the first result is concerned, constancy of production infers, of course, that the amount of distillate and waste obtained from the unit remains constant and that the quality of these products is unchanged, assuming, of course, that the requirements noted above are fulfilled.

The second result, constant conditions at any point in the system, is perhaps the chief reason why continuous distillation has been so successful, since it is possible to so design the distilling equipment as to take care of the conditions to be expected at any point in the system, since these conditions remain unchanged; that is, in the fractionating column of a continuous still, the composition of the liquid on the plates and the vapor between the plates will remain the same so long as the requirements for continuous distillation are fulfilled.

Essential Parts of a Continuous Still.—The essential parts of a unit for continuous distillation are, in general:

1. Feed heater.
2. A fractionating column.
3. Condenser.
4. Source of heat.
5. Source of cooling liquid.
6. Recuperator.

Feed Heater.—The function of the feed heater is to raise the temperature of the continuously incoming feed liquor to as near the boiling point, under the conditions obtained in the still, as is possible. This feed heater may be in several parts, depending upon circumstances. For instance, the condenser receiving the vapor from the fractionating column may be divided into several units, one or more of these units being utilized for preheating the feed liquor by allowing the feed liquor to pass through it instead of cooling water Usually, however, the temperature obtained in such a vapor heater, as it is called, is not sufficiently high and it is therefore usual to allow the partially preheated liquor to pass then to a recuperator where it receives heat from the hot waste liquor discharged from the bottom of the still, this recuperator usually raising the temperature of the feed nearly to its boiling point. In some special cases, usually when either the vapor heater or the recuperator is dispensed with for manufacturing or operating reasons, it is customary to heat the incoming feed by means of a steam heated preheater. This last method, however, is uneconomical and only used under special circumstances It is, of course, possible to run the cold feed liquor directly into the still without preheating at all. Since the feed liquor is always run into the fractionating column onto some proper plate, the heating of the liquor to boiling will take place in the column and the corresponding cooling obtained in the column will have the effect of additional dephlegmation or reflux and will therefore improve the degree of fractionation obtained from the point of entrance of feed down to the bottom of the column. Since, however, the most efficient distilling column is that one where the maximum reflux traverses the entire length of the column, the heat, thus taken out of the lower portion of such a column will be of no assistance in improving the fractionation in the upper portion of the column and it is, therefore, better practice to take care of any excess reflux required by the means of the reflux condenser and preheat the incoming feed by means of the waste heat of the vapor or the discharge from the bottom of the still.

Fractionating Column.—The fractionating column of a continuous still is in general the same as that used in the intermittent still, its design depending, of course, upon special conditions in the particular unit. Quite often in the more complicated continuous stills the fractionating column is divided into several units which are operated semi-independently of each other and some of these will be discussed later under special applications of continuous distillation.

Condensers.—In the same way, the condensing units used in continuous stills are similar to those used on intermittent stills and are designed in similar fashion. The utilization of the source of heat, however, is usually different from that of the intermittent still. In general, there are two methods of heating where steam is to be the source of heat. Where other sources of heat are used, for instance, direct fire, in general, the rules laid down for steam will apply with suitable modifications. Closed steam or steam within steam coils or pipes is usually used for nonaqueous solutions, where it is not desired to bring water into direct contact with the liquor which is being distilled, or closed steam is used for the distillation of aqueous solutions where the water is taken off as distillate and does not remain in the residue, the introduction of water vapor into the residue, of course, defeating the purpose of the distillation.

Open Steam.—The second method of heating with steam is to use open steam; that is, blowing water vapor into direct contact with the liquid in the still. This is usually used for aqueous solutions having water or other aqueous residue as the less volatile portion of the liquid which is being distilled or where the introduction of water into the less volatile product from the still will do no harm.

The second essential part of the continuous still, a fractionating column, is usually divided into two portions which are called respectively, the exhausting portion and the rectifying portion, the feed entering the column always being taken in at the dividing point between these two sections.

Exhausting Column.—The function of the exhausting column is to remove from the less volatile material discharged from the bottom of the still all of the more volatile material present in the feed, while the function of the rectifying column is to separate the more volatile component as nearly as possible from the less volatile component, discharging the more volatile component from the top of the rectifying column and the condensing steam and the less volatile component into the exhausting column.

Rectifying Column.—The rectifying column is usually placed above the exhausting column so that the reflux passing down through the rectifying column can flow by gravity into the top of the exhausting column. The design of the exhausting column depends, of course, upon the same things that were noted in the discussion of the rectifying column in the intermittent still, the number of plates to be used being a function of the relative ease or difficulty of the separation of the more volatile component from the less volatile component, a function of the composition of the feed entering the top of the exhausting column and the composition of the waste liquor discharged from the bottom. The volume of the column is a function of the time of contact desired between the liquor and the vapor, the exhausting column usually being made sufficiently great in diameter and having a sufficient depth of liquor on the plates to insure that the liquor descending through the column is in contact with the vapor a sufficiently long time so that all of the volatile component will be removed from it. The character of the plates to be used in the exhausting column is a function of the character of the liquor passing down through them; for instance, if the liquor which is being distilled contains solids as is frequently the case, the plates must be so designed that the solids will not deposit out on the plates and stop up the vapor openings.

Design of Rectifying Column.—The design of the rectifying column may be worked out on exactly the same lines specified in the case of the intermittent still, remembering, however, that the number of plates required is not a function of the ease or difficulty of separating one pure component from another pure component, but the rectifying column has to separate the more volatile component from a mixture of the composition of the feed entering the top of the exhausting column and therefore, as a rule, fewer plates would be required in a rectifying column of a continuous still than would be the case in the rectifying column of an intermittent still. Since, however, the exhausting column of the continuous still usually is designed to insure that the discharge from its bottom contains none of the more volatile component, the total number of plates in the continuous still will be greater than in the intermittent still designed for the same work.

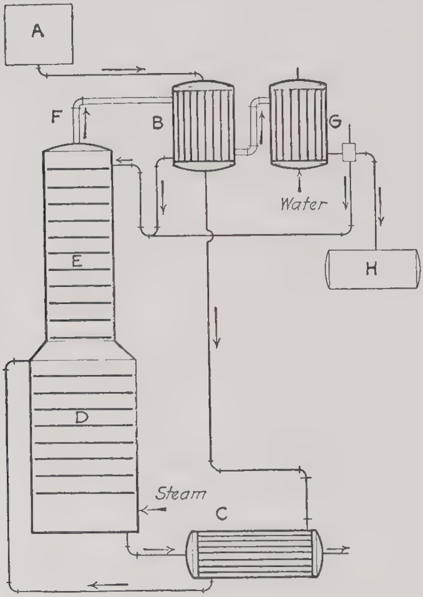


Fig. 28.—Diagram of a simple continuous still.

Diagram of Continuous Still.—The accompanying diagram, Fig. 28, will give an idea of the essential features of a continuous still for the separation into its parts of a two-component system, where *A* represents a constant level feed tank for supplying feed at uniform rate to the apparatus; *B* represents a vapor heater where the cold feed is heated part-way to its boiling point by the hot vapor coming from the top of the fractionating column; *C* represents the recuperator where the partially preheated feed is raised nearly to its boiling point by means of the hot discharge from the bottom of the fractionating column; *D* represents the exhausting column where the feed enters on the top plate and the less volatile liquid gradually runs down from plate to plate and is discharged from the bottom passing through the recuperator; *E* is the rectifying column where the vapor from the top of the exhausting column is subjected to a fractional distillation, the more volatile component being discharged through the vapor pipe, *F*, to the feed heater, *B*, and the less volatile component running back into the exhausting column; *G* is the condenser which receives the vapor which is not condensed in the feed heater, *B*, and condenses it completely, the liquid thus obtained either being run back into the top of the rectifying column together with the condensed vapor from the feed heater, or being carried off to suitable receiving tank, *H*, as indicated. Cooling water would be required for the condenser, *G*, only. In case it was necessary to cool the less volatile component discharged from the bottom of the exhausting column to a temperature below that at which it leaves the recuperator, it would be necessary to put an additional cooler on the waste line and in case the condenser, *G*, failed to cool the distillate to a sufficiently low temperature, it would be necessary to introduce a suitable cooler into the line taking the distillate from the condenser to the receiving tank. The steam used for heating the still would be introduced into the bottom section of the column, *D*, either closed or open steam being used, depending upon circumstances as noted above.

Stills for Three-component Mixtures.—Continuous stills are of particular value in handling systems containing more than two components. For instance, in three-component systems: It will therefore be interesting to discuss such a system, taking for example the actual case of the system, ethyl-ether, ethyl-alcohol, water, it being possible to separate the ether completely from the alcohol and water by fractional distillation and it being possible to obtain about a 96 per cent alcohol from the water in the same way. If we consider the 96 per cent alcohol which is the constant boiling mixture of alcohol and water to be for our purposes a pure component, spoken of as alcohol, since it behaves exactly as a pure component would, it will be possible to discuss a suitable continuous unit for separating almost completely these three components from each other.

In any continuous still for the separation from each other of three components one component is always separated first from the other two and these are also separated from each other by a subsequent operation. In the system noted above, ether, alcohol and water, it is possible to obtain the separation of the three components in several ways. For instance, in diagram, Fig. 29, *A* represents a constant level feed tank containing the mixture of alcohol, ether and water. The liquid is allowed to pass through a feed heater which, in this case, will consist of first

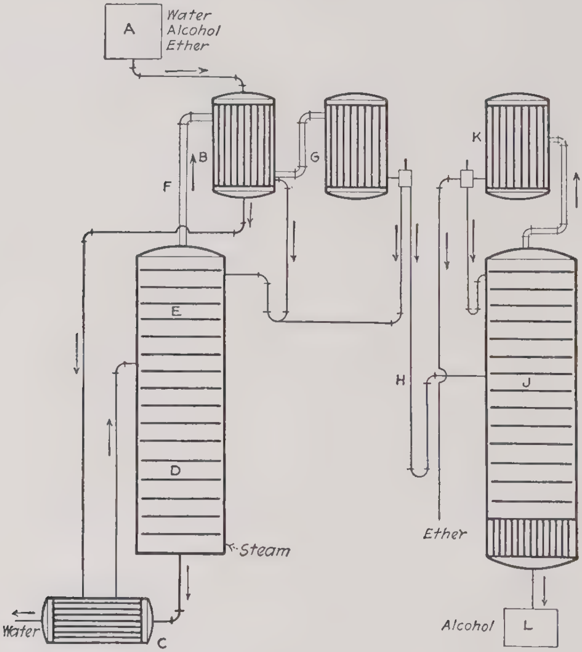


Fig. 29.—Type A—continuous still for three components.

a vapor heater, *B*, and then a waste recuperator, *C*, the heated feed then passing into the central portion of a continuous fractionating column, the exhausting section being represented by the portion *D* and the rectifying section by the portion *E*. The vapor from the top of the rectifying section passes through the vapor line *F* to the feed heater *B* and from there to the total and reflux condenser *G*. In this column the ether and alcohol are separated from the water, the water being the less volatile component and the ether and alcohol the more volatile components. The composition of the liquor approaching the bottom of the exhausting column increases in water until at the bottom, water only is obtained and hot water is discharged from the exhausting column through the recuperator to the sewer, live steam being blown into the bottom of the column to supply the vapor and heat necessary for the vaporization of the alcohol and ether.

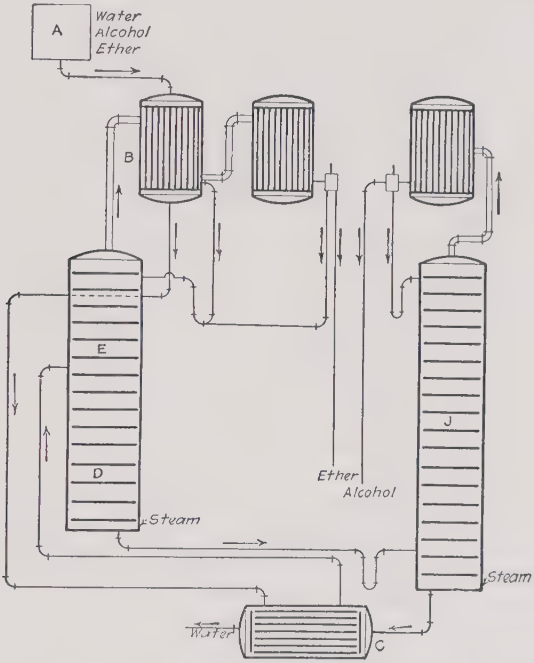


Fig. 30.—Type B—continuous still for three components.

The rectifying column *E* has the problem of separating entirely the water from the ascending vapor so that the liquid condensed in the condensers *B* and *G* consists of a mixture of alcohol and ether only. This condensed distillate then passes through the line *H* into the central portion of another continuous fractionating column *J*. This fractionating column *J* differs from the preceding column in that the source of heat at the base is not open steam but closed steam in the form of some sort of a tubular or oil steam heater. In this column there are to be separated only two components, the alcohol and the ether. The ether being more volatile passes up while the alcohol being less volatile passes down, the alcohol at the bottom being ether free while the ether at the top is alcohol free; the ether vapor being condensed by means of the condenser *K* while the alcohol is withdrawn hot from the bottom of the column and passed through a suitable cooler *L* to a receiver.

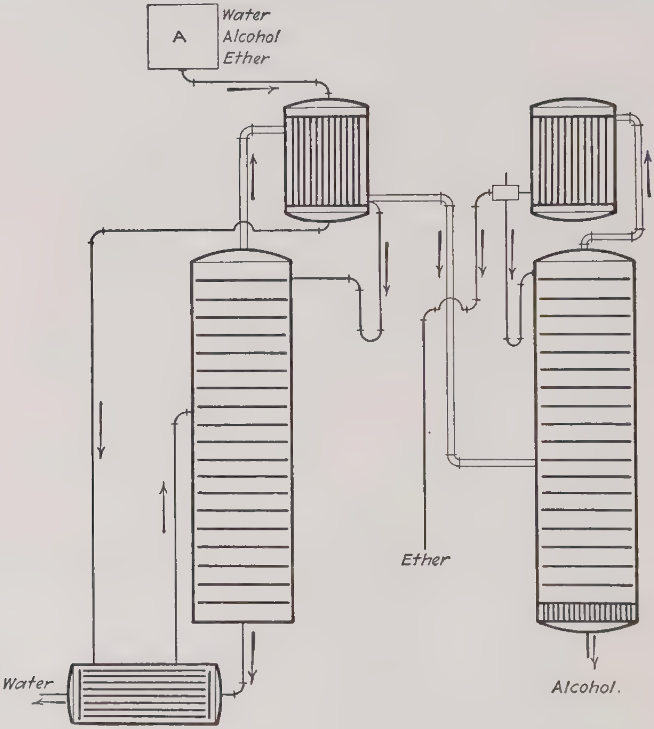


FIG. 31.—Type C—continuous still for three components.

Another method of accomplishing the same result is indicated in diagram, Fig. 30, where a mixture of ether, alcohol and water is held in a constant level feed tank *A* and flows from there through a preheater *B* to a recuperator *C* and into the central portion of the column *DE* as before, the difference being that the recuperator operates on the second column instead of the first. The column *DE* in this case separates the most volatile component, ether, from the alcohol and water, the ether passing up through the column and the alcohol and water passing down. The heat and vapor necessary for operating this column being supplied by open steam introduced at the base as before. The ether passing out of the top of the rectifying column as vapor is condensed in the condensers and is collected in a suitable ether receiving tank, while the hot liquor being discharged from the bottom of the exhausting column, which consists of a mixture of alcohol, water and condensed steam, flows by gravity into the central portion of the second column *J* where the alcohol and water are separated continuously, the alcohol going to the top and the water to the bottom as indicated.

The third method of separating the three components is indicated in diagram Fig. 31, which is similar to the diagram No. 29 except that the mixture of ether and alcohol passing from the top of the first column to the central portion of the second consists of alcohol-ether vapor instead of condensed alcohol and ether and therefore it is unnecessary to re-vaporize these liquids in the second column. It is necessary, however, to furnish a certain amount of heat and vapor in order to obtain the fractionation required in the second column and therefore a closed heater at the base of the column is used as in the first case.

Non-aqueous Solutions.—These preceding diagrams indicate the possible designs when water is one of the three components. Where the non-aqueous solutions are to be distilled the method to be followed is similar in all respects except that live steam is not introduced into the system at any point, closed heaters being used entirely. There are, however, exceptions to this rule where the material being distilled is insoluble in water and the introduction of steam into this material will not cause any harmful dilution since any water vapor which condenses in the material discharged from the column can be separated afterwards continuously by suitable decanting apparatus.

Multi-component Systems.—In the case of systems of more than three components it is usually necessary to add an additional section for each component and the systems, of course, become more and more complicated. It should be realized also that as systems become more and more complicated it is necessary to furnish so-called fly-wheels with such systems which will permit the equalization of the operation of different portions of the apparatus. Such flywheels usually consist of large intermediate receiving tanks where the liquid may be collected temporarily while subsequent units of the machine are being regulated, it being manifestly impossible to regulate all of the sections of the complicated machine at the same time.

Accessories.—The successful operation of continuous fractionating stills depends to a considerable extent upon the suitable selection of accessories. Among these accessories perhaps the most important is the so-called steam regulator which has the function of maintaining constant steam pressure automatically on the distilling column. Since the rate of distillation in a distilling column is a function of the pressure of the vapor in the column and since the quality of the product depends upon the rate at which the distillation is carried out it is essential that the steam regulator be of the highest degree of sensitiveness, and the variation in pressure in the column to a fraction of an inch of water must be noted and counteracted by the steam regulator. These regulators usually operate on the principle of the U-tube or balanced columns of liquid, the pressure on the one side of the U being maintained by the column while the pressure on the other side is usually atmospheric. The change in the relative pressures, therefore, will affect the level of the liquid in the two sides of the tube and by means of suitable floats this change in level can be made to operate control valves on the steam supply, etc. In the same way the method of controlling the feed supply and cooling-water supply is of great importance.

Feed Control.—In complicated continuous distilling apparatus, a slight change in the rate of feed often has no appreciable effect on the product of the distillation until after a considerable period of time—sometimes as much as an hour being required to detect any change in the quality of the product. It is therefore essential that the feed control be very sensitive so that the regulation may be made very exact and that very small changes in the rate of feed may be made. In handling large quantities of liquids it is essential to use large piping and large apparatus where it is very difficult to obtain careful regulation, and it is therefore customary to use the by-pass system of feed control where most of the liquid fed into the still passes through the main line through a large valve which can be opened to some point approximately correct, while the finer regulation is obtained by means of a by-pass and a needle valve which can be controlled very exactly. These valves are usually fitted with indicating devices by which it is possible to tell by inspection the degree of opening of the valves.

Testers.—The products obtained from the apparatus also must be under constant observation. This is usually accomplished by means of overflow devices which are called testers. These testers usually consist of glass bell jars or other designs of a similar nature where the distillate flows continuously through an opening, the rate of discharge often being measured by the level of liquid passing through a weir under the bell jar. It is also possible to observe the quality of the distillate continuously in such testers where the specific gravity of the liquor is a measure of its quality by having suitable hydrometer arrangements within the testers so that the specific gravity reading may be observed at any time.

Slop Testers.—The waste liquor discharge from the bottom of the still is usually tested by a device known as the slop tester which takes the vapor from a section near the bottom of the exhausting column and condenses this vapor by means of a small condenser in such a way that the condensed vapor flows through a small hydrometer tester where its specific gravity can be observed continuously. These testers, feed valves, steam regulators, etc. are usually located at one point so that the operator in charge of the machine is able to operate all the controls and observe the operation of the machine without moving from one position.

Advantages and Disadvantages of Continuous Distillation.—Continuous distillation has numerous advantages and also has certain disadvantages. In general, the advantages may be classed under three headings:

1. Uniform quality and high grade of product.
2. Heat economy.
3. Labor saving.

The uniformity of the quality of the product and the high grade which can be obtained is due to the fact that the continuous still operates with uniform conditions at all points in the system and it is therefore possible to design the system in such a way that impurities may be taken care of much more satisfactorily than can be done in the case of the intermittent distilling apparatus, where the quality and quantity of a product varies continuously during the distillation of each successive batch.

The heat economy obtained in the continuous still comes from two sources. In the first place, the heat required to raise the liquor to the boiling temperature is usually recovered in the continuous still by suitable heat interchangers, whereas in the intermittent still, all this heat is lost, and in the second place, the production of large amounts of intermediate fractions which must be re-distilled in order to recover from them valuable constituents means that a large amount of heat must be supplied for this purpose. In the same way, the labor saving on the continuous system is effected in that there are no intermediate fractions to be redistilled. There is no labor in connection with filling and emptying and cleaning out kettles and the operation involves very little attention after the machines have been suitably regulated, one operator usually being able to care for a number of continuous stills without undue exertion.

The disadvantages of the continuous system, however, are sometimes serious. They are in general:

1. Excessive first cost.
2. Sensitiveness to external conditions.
3. Complicated construction and operation.

The excessive first cost of the continuous system lies chiefly in the fact that the accessories necessary to permit automatic operation are frequently complicated and expensive, and while the fractionating columns usually are similar to those used in intermittent stills and there usually is no distilling kettle, the steam regulators, slop testers and other accessories frequently increase the cost of the equipment considerably. Also, the continuous still is very sensitive to external conditions. As has been noted above, the continuous still operates successfully only where the quality and quantity of liquor fed to it is uniform and when steam and water supply remain constant, and, if in the operation of the process producing the material to be distilled there are changes from time to time, where the material to be handled is variable, then the continuous still usually must undergo certain modifications in its design in order to handle the change in material, whereas in the case of the intermittent still it is usually possible to handle in a more or less satisfactory manner almost any material of nature similar to that for which the still was designed.

Finally, the continuous system is complicated in construction and the operation requires a man trained for the work, and since frequently the operation of distilling equipments must be entrusted to relatively unskilled labor, continuous stills are frequently avoided on this account. In general, however, it may be said that other things being equal, the continuous still is much to be preferred.

CHAPTER XVII

AMMONIA

The problem of manufacture of pure anhydrous ammonia from crude ammonia liquor obtained from gas works is one of the most interesting and also complicated problems with which the distillation engineer has to deal.

Sources of Ammonia Impurities.—Crude ammonia obtained from the destructive distillation of coal contains besides ammonia and water, a large number of other impurities consisting chiefly of compounds of carbon, sulphur and nitrogen. These impurities are frequently combined together in the form of such compounds as ammonium sulphide, ammonium carbonate, ammonium cyanide, sulphur combinations of the above and various organic nitrogen compounds such as pyridene bases and other objectionable smelling substances of this type. There is a certain amount of tarry matter of the general nature of coal tar present in the crude ammonia liquor. Part of the ammonia in the crude liquor is present as free ammonia or ammonia hydroxide which can be completely removed from the solution by boiling while the balance of the ammonia may be present as so-called fixed ammonia; that is, combined with some of the other substances in such a way that some treatment more vigorous than boiling is necessary to drive it out of solution. Most of the organic nitrogen compounds are in this class, it being usually necessary where these are abundant to combine with the boiling the action of a strong base, together with reducing agents of a suitable sort. In general, however, the process of recovering all of the ammonia from the crude liquor consists of boiling the liquor in the presence of milk of lime which decomposes most of the fixed nitrogen compounds in such a way that practically all of the nitrogen available is driven off as ammonia. A part of the impurities present in the solution, however, are volatile and are driven off with the ammonia during this process, and the equipment required to produce pure anhydrous ammonia, therefore, must have provision for the removal of these impurities which may be classed for practical purposes as hydrogen sulphide, carbon dioxide, pyridene and tar. The hydrogen sulphide and carbon dioxide are usually present in the liquor as ammonium sulphide and ammonium carbonate. Both of these compounds, however, are stable only at low temperatures and decompose at the boiling temperature, giving off in the vapor, hydrogen sulphide, carbon dioxide and ammonia. It is also true that the hydrogen sulphide and carbon dioxide are less soluble in water than the ammonia. Therefore, at any given temperature the partial pressure of the hydrogen sulphide and carbon dioxide in the vapor phase of equilibrium with the liquor will be greater than that of the ammonia. By properly arranging a machine, it is possible to get a fairly complete separation of the two volatile gases from the more soluble ammonia by control of temperature and concentration.

The pyridene bases and the tarry oils which are present in small amounts in the ammonia can usually be removed by partial condensation of the vapor where some of the oils will condense out and can be decanted and by washing the vapors with some suitable relatively non-volatile petroleum oil in which the pyridenes are soluble and which will wash them out of the ammonia water vapor.

The bulk of the impurities having been removed by the above methods, the last traces of the hydrogen sulphide and carbon dioxide can usually be removed by passing the vapor through solutions of caustic soda which will combine with them and render them non-volatile.

Diagram of Continuous Ammonia Still.—The small amounts of tarry material present are usually removed by absorption on activated charcoal. A very large number of designs have been utilized for the removal of pure ammonia from crude liquor. In general, it has been found that the continuous system of distillation is the most satisfactory and the accompanying diagram, Fig. 32, will give an idea of how this system may be utilized for this purpose.

A represents a feed tank for feeding continuously the crude ammonia liquor to the system. This liquor first is preheated by means of a vapor heater *B* and then it passes into the central portion of a continuous distilling column *EF*. The columns used in ammonia stills are quite different from those used in the distillation of the finer products such as alcohol, ether, acetone, etc. In the first place, all apparatus to be used in connection with ammonia must be made of steel or cast iron. It is therefore necessarily of more or less massive nature. Furthermore, owing to the possibility of the formation of solid ammonia compounds with the carbon dioxide and hydrogen sulphide there is always the possibility of clogging of the equipment. Therefore, if the plate type of fractionating column is to be used, the caps are made large with serrated edges and little attempt is made to obtain the intimacy of contact which is desired in the finer types of distillation equipment.

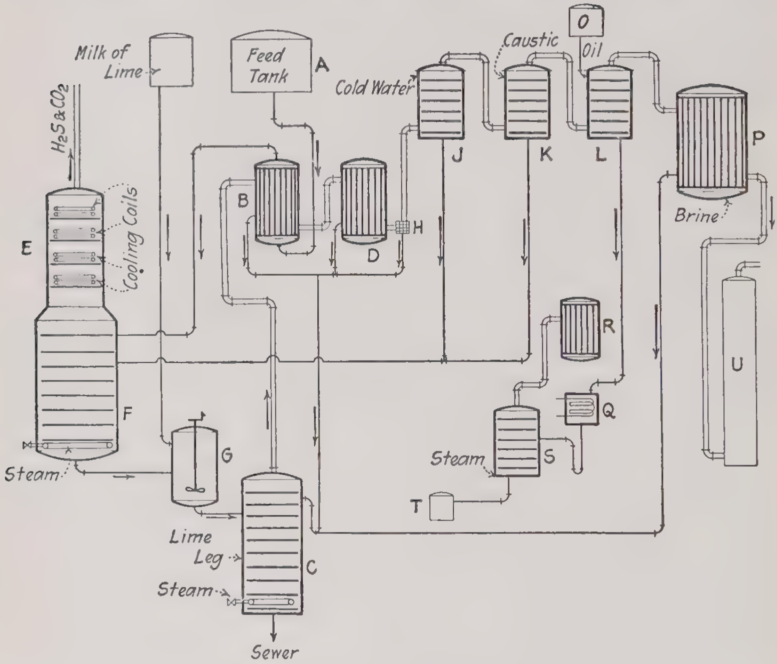


FIG. 32.—Continuous ammonia still.

Removal of Hydrogen Sulphide and Carbon Dioxide.—All parts of the ammonia system are constructed so that they may be opened up for cleaning at any time and everything is made as accessible as possible. The continuous column, *EF*, is divided into two parts, the upper part *E* consisting of a number of plates on which there are a number of coils containing cooling water, while the lower part *F* is heated by the introduction of open steam. The crude ammonia liquor running down over the plates of the column *F* comes into contact with the open steam and the volatile hydrogen sulphide, carbon dioxide and ammonia are driven out. Since, however, the hydrogen sulphide and carbon dioxide are less soluble at any given temperature than the ammonia, the two former are driven out more readily and therefore the vapors passing up through the upper column *E* contain a larger percentage of these gases than is found in the entering feed. The vapors passing up through this column come into contact with the cooling coils whereby they are partially condensed so that if the temperature at the top of the column *E* is kept sufficiently low, the gases escaping from the top of the column consist almost entirely of carbon dioxide and hydrogen sulphide and practically none of the ammonia is carried off with them. It is, therefore, usually customary to exhaust these gases directly to the atmosphere and the loss of ammonia with them is very small indeed. It should be noted, however, in connection with these exhaust gases that both hydrogen sulphide and carbon dioxide are very dangerous gases and should be exhausted outdoors at such a point that they will not be likely to collect and become dangerous.

Treatment with Lime.—The liquor passing down through the column *F* and being diluted by the introduction of steam used for boiling, then passes out through the bottom into a mixing tank *G* where it is mixed with suitable quantity of milk of lime which is supplied from the feed tank *M*. The mixture of ammonia liquor with milk of lime then runs into the exhausting column *C* where it is boiled by the introduction of live steam into the bottom section. This lime leg, as it is called, must be designed so that the solid particles of calcium hydrate will find no opportunity to become lodged on the plates of this column so that it would be clogged up. The column also must be made very accessible for cleaning on account of this danger. The lime in contact with the ammoniacal liquor at the high temperature is freed of all of its ammonia, which escapes from the top of the column through the vapor pipe as indicated, while the excess lime, together with the non-volatile material is discharged in the sludge from the bottom of this exhausting column to the sewer.

Removal of Oils.—The vapor from the lime leg passes first to the reflux condenser which is used as the preheater *B* and then to a second reflux condenser *D* where it is cooled by cooling water to a fairly low temperature. It has been found that certain oils which are present in the ammonia will condense out at this point in the purification so that the liquor discharged from the condenser *D* if passed through an oil decanter *H* will have removed from it a considerable portion of these insoluble compounds. The decanted liquor then running back into the top of the exhausting column as indicated.

Scrubbers.—The ammoniacal vapor now freed of nearly all of the hydrogen sulphide and carbon dioxide and of a certain amount of oils passes into a compound washing or scrubbing tower indicated by the tower *J*, *K*, and *L*. This column is divided into three sections. In the first section *J*, the gas is washed by water which removes from it a number of impurities which have escaped previous purifying processes. This water, of course, coming into contact with strong ammonia dissolves a large amount of the gas and the heat of solution is such that the water would be raised to a higher temperature were it not for the fact that cooling coils are supplied on the plates of the column. The wash water obtained from this column then is allowed to flow back into the central portion of the column *F* as indicated so that the ammonia thus dissolved of the water is not lost. The gas then passes to the second section where it is washed by a dilute solution of caustic soda which neutralizes all of the remaining hydrogen sulphide and carbon dioxide, forming nonvolatile sodium carbonate and sodium sulphide, the caustic liquor being allowed to return to the column *F* together with the liquor from the water scrubber *J*. The vapor now freed from the gases passes into the oil scrubber *L* where it is washed with a suitable petroleum oil which dissolves out of the gas all of the soluble pyridene bases, thus removing all of these objectionable smelling pyridenes. The oil from this scrubber, containing but little ammonia, can be used over again, and it is therefore customary to take the oil through a steam heated oil preheater *Q* into an oil exhausting column or oil leg *S* as indicated, where it is boiled by the use of open steam, driving off the pyridene which is condensed in the condenser *R*, while the oil freed from pyridene is discharged from the base of the column into a cooler and oil supply tank *T*, from which point the oil feed tank *O* shown above is supplied.

Removal of Water.—The vapor from the oil scrubber *L* now containing only water and a small amount of tarry impurities passes to a condenser *P* where it is brought into direct contact with brine, the brine condensing out of the ammonia gas nearly all of the water vapor present. The condensed product, ammonia liquor, obtained is allowed to run back through pipe lines indicated into the top of the exhausting column *C* where the ammonia is handled over again, while the gas now practically water free is allowed to pass into an ammonia tower *U* where it is brought into direct contact with lumps of solid caustic soda which remove from it all of the rest of the water vapor down to the vapor pressure of water which is in equilibrium with solid caustic soda at that low temperature. The ammonia gas is then passed through one or two towers filled with activated charcoal, usually animal charcoal, which has the property of absorbing all of the tarry material present, recovering the gas escaping from these scrubbers, practically pure ammonia. This ammonia is then carried to ammonia compressors where it is compressed cooled and liquefied.

CHAPTER XVIII

BENZOLIZED WASH OIL

It is common in the industries to find gaseous mixtures which contain certain condensable vapors which must be separated from the rest of the mixture. Such mixtures as coal gas from the destructive distillation of bituminous coal, and gases from solvent recovery systems, are illustrations of this class of gases. In the former case there is ammonia, which is removed from the coal gas by washing with water, or by passing the gas through sulphuric acid. Coal gas also contains benzene and its homologues, which can be washed out of the gas by the use of any relatively non-volatile oil in which the benzene is soluble. In the latter case, the gases may contain such vapors as ethyl alcohol which is soluble in water and may be readily washed out by it, or the gases may contain such vapors as gasoline or benzol, in which case they can be washed out by some suitable solvent such as oil, as before. It is the case of the vapor which has been dissolved in the relatively non-volatile oil, which will be discussed.

Light-oil Recovery.—Gas plants which recover the "light oil" (benzene and its homologues) usually do so by scrubbing the gas in tall towers down through which the "wash oil" (in this country, wash oil is usually a petroleum oil of high boiling point) is allowed to pass in countercurrent contact with the ascending gas. The wash oil leaving the bottom of the scrubbing tower is, therefore, more or less saturated with the light oil at the partial pressure at which the gas enters the scrubber. This so-called Benzolized Wash Oil must then be subjected to a process of fractional distillation in order to recover the light oil and to render the wash oil fit to be used again in the scrubbing process.

Wash Oil.—The grade of petroleum distillate used for scrubbing may be considered to have a boiling point at atmospheric pressure of about 300°C. In order to study the problem of handling this material, it is advisable to have a boiling point-pressure curve for this material. One method of doing this where the actual vapor pressure data is not available is to make use of the modified Clapeyron Equation noted in a previous chapter

$$\frac{dp}{dT} = \frac{L}{RT^2}$$

which integrated gives the equation

$$\ln p = -\frac{L}{RT} + \text{constant}$$

For a straw petroleum oil of boiling point 300°C., L may be estimated as 11,750 calories giving

$$\ln p = -\frac{5,910}{T} + 16.95$$

where p is in millimeters of mercury and T is degrees Centigrade absolute.

The vapor pressure curve of Benzene has been determined and the relative pressures of Benzene and Wash Oil are given in the following table:

Temperature, degrees Centigrade	Vapor pressure of benzene in millimeters	Vapor pressure of wash oil in millimeters (calculated)
80	760	1.22
100	1,344	3.02
150	4,334	19.7
200	10,663	85.5
250	22,214	282.0
300	40,000	760.0

Boiling-point Curve for Mixture of Benzol and Wash Oil.—It is possible by assuming Raoult's Law to hold, to get an approximation of the boiling point curve of mixtures of Benzene and Wash Oil.

Thus on the diagram, Fig. 33, the line *AD* represents the partial pressure of Benzene in the mixture at some given temperature t, while *CB* is that for wash oil, and the line *CD*, the sum of the two partial pressures, or the total pressure. If x represents the mol fraction of the benzene in the mixture the total pressure will be given by the equation.

$$P = P_w + x(P_B - P_w)$$

Thus at different temperatures the mol fraction of Benzene in the mixture boiling at a given pressure can be calculated.

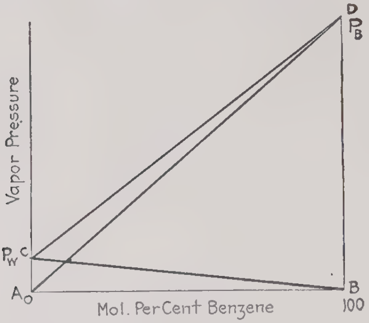


FIG. 33.—Vapor pressure relations. Benzene—wash oil mixtures.

The following table gives the results of such a calculation for a pressure of 760 mm.

Temperature, Degrees Centigrade		
80	$P = 760 = 1.22 + x(760 - 1.22)$	$x = 1.000$
100	$P = 760 = 3.02 + x(1{,}344 - 3.02)$	$x = 0.563$
150	$P = 760 = 19.7 + x(4{,}334 - 19.7)$	$x = 0.172$
200	$P = 760 = 85.5 + x(10{,}663 - 85.5)$	$x = 0.064$
250	$P = 760 = 282.0 + x(22{,}214 - 282.0)$	$x = 0.022$
300	$P = 760 = 760.0 + x(40{,}000 - 760.0)$	$x = 0.000$

The partial pressure of the benzene in the vapor above such mixtures may then be calculated and the mol fraction in the vapor phase.

$$pp_B = x\,P_B \text{ and}$$

$$x_{\text{vapor}} = \frac{pp_B}{P}$$

For the temperatures selected the following table can be thus obtained.

Temperature, degrees Centigrade	x liquid	pp_B	x vapor
80	1.000	760	1.000
100	0.563	757	0.997
150	0.172	745	0.981
200	0.064	684	0.899
250	0.022	488	0.642
300	0.000	0	0.000

Temperature-composition Diagram.—It is now possible to construct a temperature-composition diagram, Fig. 34, for mixtures of Benzene and Wash Oil at 760 mm. pressure.

It is evident from such a diagram, that the two components are very readily separated from each other, a dilute solution of 2 mol per cent benzene giving a vapor containing over 60 mol per cent. Such a solution would boil at 250°C. In order to thoroughly remove all the benzene from the wash oil by boiling at 760 mm., the temperature must be raised to 300°C.

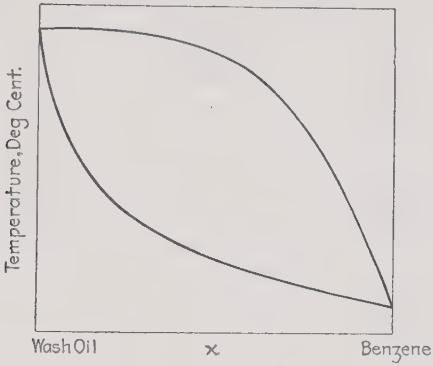


Fig. 34.—Boiling point curve. Benzene—wash oil mixtures.

Vacuum Wash Oil Still.—A still to handle wash oil at 300°C. would need a fire-heated kettle, or else hot oil must be used, since saturated steam would require too high a pressure, and superheated steam is not a satisfactory agent for heating on account of the high resistance to flow of heat from it to metal. Fire heat is, however, dangerous, and is likely to decompose the oil in the kettle, while oil heating is often expensive and troublesome. It is therefore advisable to operate this still under as high a vacuum as possible, for instance, 28 in. Hg. (50 mm., absolute pressure).

The boiling point of wash oil at 50 mm. may be calculated from the previous equation and will be found to be 180°C., while Benzene at the same pressure boils at 12°C. However, 180°C. corresponds to 130 lb. gage steam pressure which is still high, and, furthermore, in order to condense the benzene vapor, cooling water below 12°C. must be available, which is not common in warm weather. These difficulties can be avoided, however, by the use of open steam injected into the boiling mixture of benzene and wash oil, thus converting the system from one of two to one of three components. Water is practically insoluble in both benzene and wash oil and there will, therefore, appear two liquid phases, thus limiting the degrees of freedom of the system to two as before, so that fixing the pressure and the composition of the benzene wash oil phase will fix the boiling temperature of the mixture.

Since the water is practically insoluble in the other two components, their partial pressures at any temperature will remain practically unchanged, and therefore the presence of the water or water vapor will have little effect upon the problem of fractionation. The total pressure is then the sum of the partial pressures of the benzolized wash oil and the water, and by regulating the amount of steam introduced, the temperature needed for operation may be lowered the amount desired. Such a steam distillation may be carried out at atmospheric pressure. In such case the mixture of wash oil and water in the kettle of the still would boil at a temperature slightly less than 100°C. The vapor passing from the fractionating column to the condenser would consist essentially of benzene and water vapor at atmospheric pressure, and it would be necessary to cool these vapors down to a temperature somewhat below the boiling point of pure benzene in order to condense them. The weight of steam needed to vaporize a pound of benzene would be the ratio of the vapor pressures at that temperature times the ratio of their molecular weights.

Steam Consumption of Vacuum Stills.—The question whether or not the use of a vacuum steam distillation would affect the ratio of water vapor to benzene vapor in the mixture of vapors passing to the condenser depends upon the relative changes in vapor pressures with the temperature. The following table will indicate how these vapor pressures vary.

Temperature, degrees Centigrade	Water, millimeters	Benzene, millimeters	Ratio B/W
100	760	1,344	1.77
80	355	754	2.12
60	149	389	2.61
40	55	181	3.29

It is evident from this table that if the total pressure be so regulated that the mixture of water vapor and benzene vapor come over at 40°C., about one-half as much steam will be needed per pound of benzene as if the steam distillation were carried out at 100°.

There is another economy in the use of steam distillation under a vacuum. It is always necessary to heat the benzolized wash oil up to its boiling point before injecting it into the still. This may be partly accomplished by means of heat interchangers, utilizing the waste heat in the debenzolized oil, but high-pressure steam is always necessary to complete the preheating. It is obvious that the higher the vacuum at which the still operates, the lower the temperature to which the oil must be heated will be, and the less the steam pressure required for such heating. There are other reasons, such as freedom from leaks outward, safety, etc. which make the use of a vacuum in the wash oil still highly desirable.

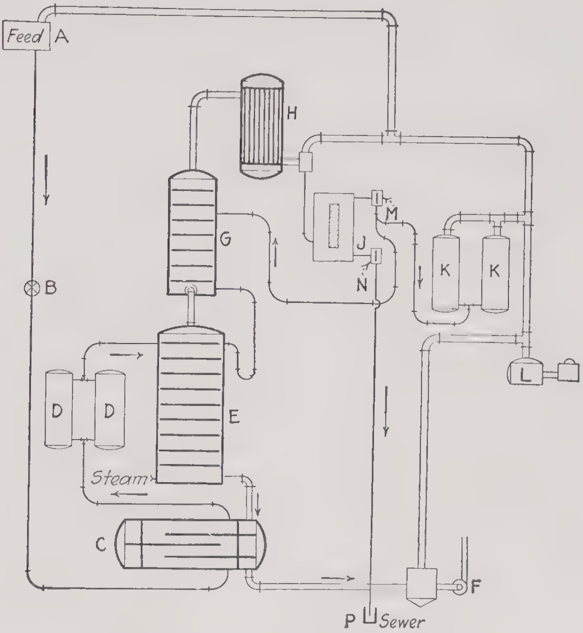


FIG. 35.—Vacuum wash oil still.

Diagram of Wash Oil Still.—A diagram of a vacuum wash oil still operating on this principle is shown on Fig. 35.

Benzolized wash oil is held in a constant level feed tank *A*, the tank being under the vacuum of the still proper to insure constant rate of feed. From this tank it flows through the regulating valve *B* to the heat interchanger *C* where it is heated counter current by the hot debenzolized oil issuing from the still. The partially heated oil then is heated to its boiling temperature in the high pressure steam preheaters *D*, two of these being furnished so that one may be cleaned without shutting down the still. The hot oil then flows to the top of the exhausting column *E* where the benzol is boiled out of the wash oil by means of steam blown into the bottom of the column. The exhausted oil passes from the bottom of the column through the heat interchanger *C*, and then is pumped out against atmospheric pressure by the pump *F*, after which it is cooled, the naphthalene removed by settling, and is then ready for re-use.

The fractionating column *G* serves to hold back the heavy oil, receiving its reflux from the regulating bottle *M*, which is attached to the continuous decanter *J*. This decanter separates the condensed water from the condensed benzol coming from the condenser *H*. The water flows from the decanter through the tester *N* through a barometric seal to the sewer *P*. The benzol is collected in the receiving tanks *K*, from which it is alternately withdrawn by breaking the vacuum on them. The dry vacuum pump *L* completes the apparatus, except for the usual accessories common to all continuous stills.

CHAPTER XIX

METHYL ALCOHOL

Methyl alcohol is obtained almost exclusively from the destructive distillation of cellulose material, usually hard woods. Associated with it in the distillate condensed from this process are a large number of other substances; notably, water, acetic acid and acetone, together with smaller amounts of a large number of other substances. The problem of the preparation of pure methyl alcohol from this mixture is unquestionably one of the most difficult that the designer of distillation equipment has been called upon to solve, and the solution was not satisfactorily completed until the introduction of the modern continuous still.

Impurities in Wood Alcohol.—Acetic acid and the other organic acids present, are, in general, neutralized with lime or some other suitable alkali, thus rendering them non-volatile. The alcohol, acetone, and the balance of the volatile material are then separated from the salts by a simple distillation. The distillate thus obtained is known as crude wood spirit and has a composition of which the following is an example.

Methyl Alcohol	55 to 50 per cent
Acetone	12 to 14 per cent
Other impurities	5 to 10 per cent
Water	28 to 26 per cent

The other impurities consist principally of the following substances:

- Aldehydes
- Methyl Acetate
- Ammonia
- Amines
- Higher Ketones (Methyl Ethyl Ketone, etc.)
- Allyl Alcohol
- Wood Oils (High-boiling, insoluble, complex substances)

Constant-boiling Mixture of Methyl Alcohol and Acetone.—Methyl Alcohol can be separated from water by fractional distillation. This is also true of acetone; but methyl alcohol and acetone together form a binary mixture of minimum boiling point which contains approximately 15 per cent alcohol and 85 per cent acetone. The respective boiling points at 760 mm. pressure are

Methyl Alcohol	66.5°C.
Acetone	56.5°C.
Constant boiling mixture	55.93°C
Allyl Alcohol	97.°C.

It is therefore impossible to produce a pure acetone from the crude wood spirit by fractional distillation without the addition of some new substances which will modify the respective vapor pressures of the alcohol and acetone in such a way that the constant boiling mixture is destroyed. This may be done by introducing into the mixture some material like Calcium Chloride, which combines chemically with the methyl alcohol, thus lowering its vapor pressure, or by some material like Sodium Hydrogen Sulphite, which combines chemically with the acetone, which can then be removed from the solution as a crystalline addition compound, and the alcohol fractionated afterwards.

"Methyl Acetone."—The demand for acetone in the past has largely been for its use as a solvent, excepting, of course, the great demand for pure acetone as one of the solvents of Cordite smokeless powder, and since the constant boiling mixture, consisting of 85 per cent acetone, is also an excellent solvent and behaves physically like a pure compound, the latter has satisfied the demands of the trade, and it has therefore been marketed under the name of methyl acetone. The problem to be solved, therefore, consists in the separation of pure methyl alcohol and pure "methyl acetone" from water, and from the other impurities. This is essentially a three component system, and as described under that subject, it is necessary to remove one component first and separate the other two afterwards. The method adopted here is to separate the methyl acetone (together with the volatile head products) from the alcohol and water, separate the alcohol from the water, and then finally separate the volatile heads from the methyl acetone.

Diagram of Still.—This method is utilized in the apparatus shown diagrammatically on Fig. 36, with the omission of a number of necessary accessories in order to simplify the drawing.

The function of the double column E_1E_2 is to separate the feed into two portions, one, containing the volatile heads and the methyl acetone, and the other the alcohol and water. The heads are delivered from the tester H to the bottom of the column G_1, while the alcohol and water are delivered from the bottom of the column E_2 to the top of the exhausting column F_2. There is an accumulation of insoluble oils in the column E_1 and they are removed by means of a continuous decanter at D, just as fusel oil is removed in the rectification of ethyl alcohol as described under that heading.

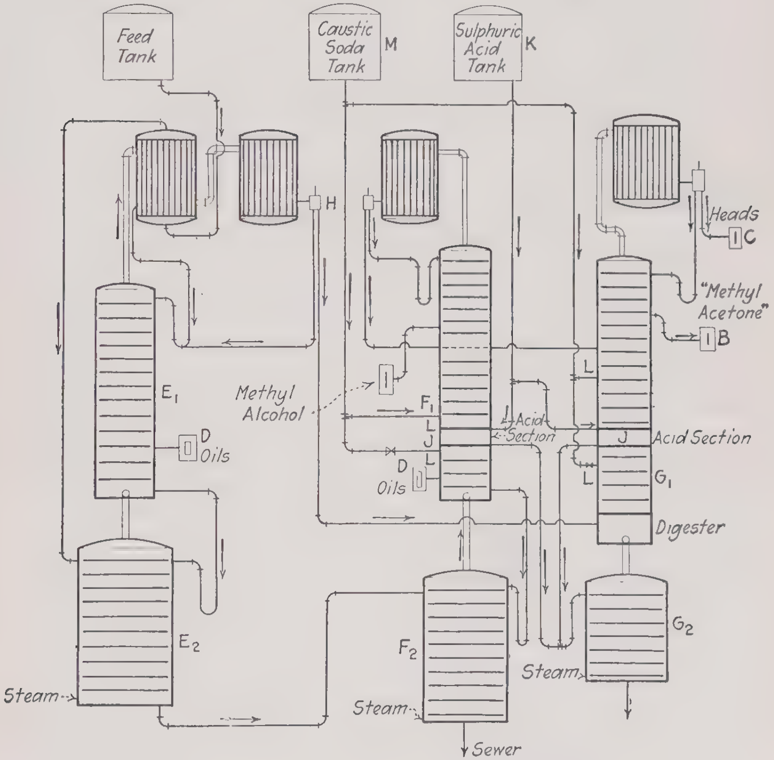


Fig. 36.—Continuous methyl alcohol-acetone still.

The function of the column F_1F_2 is to produce pure methyl alcohol and discharge to waste, the water and any non-volatile substances which may be present. The liquor entering the top of F_2 contains a small amount of heads not removed by the column E_1E_2. These heads consist of ammonia, amines, aldehydes, nitrites, and ethyl acetate. In order to handle them, there is a special section J inserted in the column through which a constant stream of dilute sulphuric acid is flowing from a storage tank K. The vapors passing up through the column bubble through this acid, thus neutralizing and rendering non-volatile the ammonia and amines and tending to polymerize the aldehydes. The reflux down through the column is by-passed around this section so the two liquids do not mix. The spent acid is taken to a sulphuric acid exhausting column G_2, where any valuable materials are boiled out of it and pass up into the column G_1.

The vapors rising through the column F_1 above the acid section J contain a small amount of acid, and this is then neutralized by introducing into the column at the point L, dilute sodium hydroxide from the storage tank M. This caustic mixes with the reflux, neutralizes the acid, and saponifies the ethyl acetate and nitrite. The vapors are now substantially freed from impurities in the form of heads, but in order to insure as complete removal as possible, the methyl alcohol is withdrawn "pasteurized" from the upper portion of the column (as described under ethyl alcohol), and the heads thus liberated are taken to the central portion of the column G_1 in order to recover the alcohol present in them.

The bottom section of the column G_1 consists of a sort of digester where the heads from the column E_1 are treated with boiling dilute caustic soda. The vapors rising from this digester pass up through an acid section similar to that in column F_1 and are then treated with caustic at a higher point. The purified methyl acetone is then withdrawn pasteurized through the cooler and tester B, while any remaining heads accumulating in the upper portion of the column are distilled off and collected at C. The waste sulphuric acid from the column G_1 is withdrawn to the sulphuric acid exhausting column G_2, as before.

Wood oils collect in the column F_1 and are withdrawn through a suitable oil decanter at D as in the case of the column E_1.

The feed material is therefore separated by this apparatus into pure methyl alcohol, pure constant boiling mixture (methyl acetone), concentrated head products, wood oils, and waste. This is completed in one operation, with a minimum of labor and heat, and the products are of a degree of purity unobtainable by any intermittent process of fractional distillation.

CHAPTER XX

ETHYL ALCOHOL

The fractional distillation of Ethyl Alcohol is the classical example in the art of distillation. Nearly all the technical books on the subject of distillation deal practically exclusively with the problem of producing ethyl alcohol from its various sources, and the problem has unquestionably received more thought than any other phase of the subject.

Sources of Ethyl Alcohol.—Ethyl alcohol is obtained almost wholly from the fermentation of various sugars, as are found in such materials as molasses, hydrolyzed starch, and waste liquor from sulphite pulp digesters. The conditions under which fermentation of these sugars must be carried out, are such that the alcoholic product usually contains from five to ten per cent of alcohol. This mash as it is usually called contains in addition to the alcohol and water, considerable solid material in suspension, dissolved salts of various kinds, and a number of more or less volatile substances which are by-products of the fermentation. The solid materials and the non-volatile salts can be readily removed by a simple distillation. The volatile impurities are, however, much more difficult to care for.

It has been the object of manufacturers of stills, to produce a commercial alcohol of as high a degree of purity as possible. It has only been recently, however, that the introduction of the continuous still has permitted the production of a really high grade material. Continuous alcohol stills of the type perfected by Barbet are capable of producing continuously and economically, alcohol of a high and uniform degree of purity. These stills will be modified in the future, as the action of the component parts are studied. The art of still building has suffered in the past from the fact that the problems involved have been studied empirically. The applications of physical chemistry in the future will be sure to be of great assistance in the solution of these problems.

Beer Still.—The first process in the production of alcohol from the mash is the removal of all of the non-volatile material, and a good portion of the water. This is usually carried out in what is known as a Beer Still, which is a simple continuous still of the type indicated in Fig. 37.

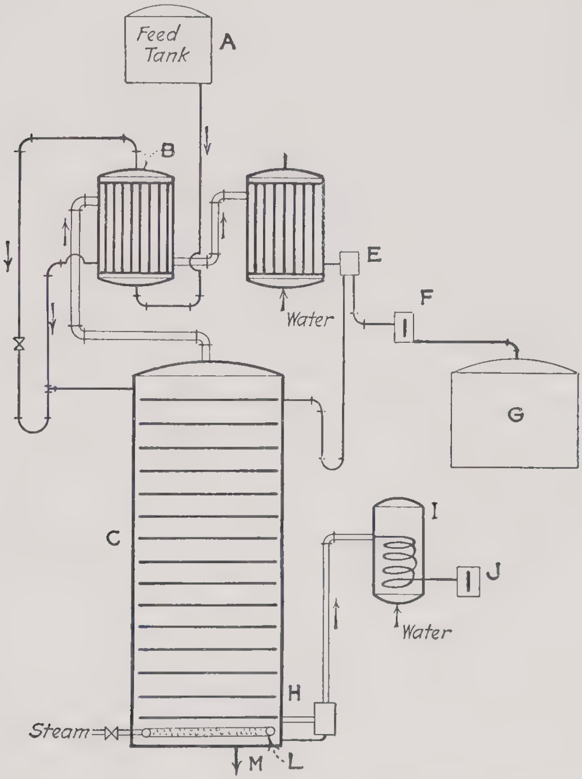


FIG. 37.—Beer still.

The alcoholic feed is supplied by a constant level feed tank *A*. This tank contains a ball float which operates a steam pump which pumps the feed from the storage tank to *A* as rapidly as it is used. The feed then flows by gravity through the feed heater *B* where it is raised nearly to its boiling point. Continuous stills are often fitted with recuperators where the incoming feed is heated by the outgoing hot waste from the bottom of the exhausting column. Where the liquor contains solid materials that are likely to form deposits on the heating surfaces, recuperators are not used, on account of the difficulty of cleaning outside of the tubes. The vapor heater shown at *B* has the liquor only inside of the tubes, and the fouled surfaces can be very easily cleaned by removing the top and bottom heads of the heater, and running cleaning devices through the tubes.

The hot feed, then, is introduced into the top section of the exhausting column *C* where it flows down from plate to plate, the volatile materials being gradually removed as it comes into contact with the steam blown in at the bottom through the perforated sparger pipe *L*. The exhausting column usually has from 12 to 15 plates, each plate being large and deep to give a long time of contact of the feed in the column in order to insure complete removal of the volatile substances. The complete removal of these substances can be readily tested by what is known as the slop tester. Vapor is withdrawn from a plate near the bottom at *H*, any liquid removed by the separating bottle, and then the vapor is condensed in a suitable condenser *I*, from which it flows to a tester *J* where it can be tasted, or its specific gravity measured by means of a hydrometer. The exhausted liquor then is discharged from the bottom of the still through a suitable seal pipe *M*. The rate of introduction of steam into the column is governed by means of a suitable pressure regulator.

The vapor leaving the exhausting column for the heater is substantially in equilibrium with the liquid on the top plate of the column. Partially condensed in the heater, it suffers enrichment in its alcohol content, and then it passes to the condenser where it is completely condensed. The vapor condensed in the heater is returned to the top plate of the column together with a greater or lesser portion of the vapor condensed in the condenser, from the regulating bottle *E*. The distillate flows through the tester *F* where its volume and specific gravity may be measured, to the storage tank *G*. On account of the partial condensation in the heater, the distillate from the 5 to 10 per cent mash will frequently run as high as 30 to 40 per cent alcohol.

The water supply for the condenser is obtained from the constant level feed tank *N*.

Crude Alcohol.—A sample analysis of such a distillate obtained from a molasses mash showed, in addition to the alcohol and water, the following impurities:

	Per cent
Organic acid measured as acetic acid	0.152
Esters measured as ethyl acetate	0.071
Aldehydes measured as acetaldehyde	0.015
Furfurol	0.00019
Higher alcohols measured as iso-amyl alcohol	0.412
Nitrogenous substances measured as ammonia	0.0006

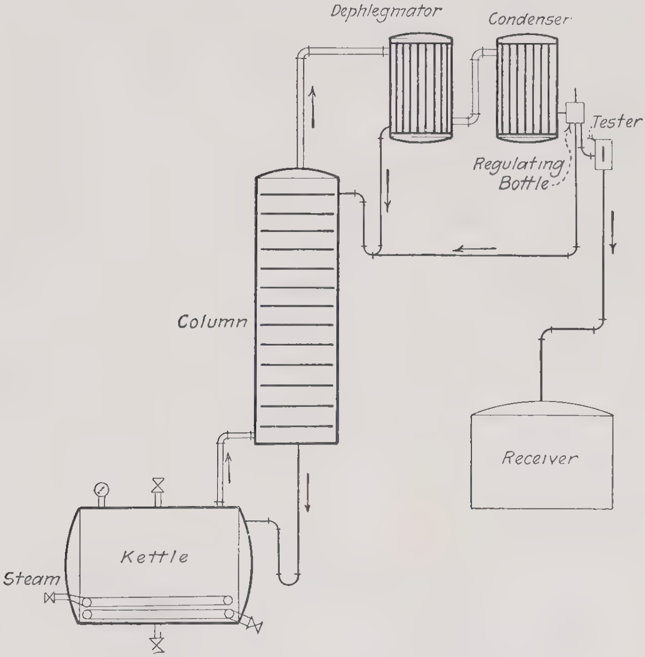


Fig. 38.—Modern intermittent still.

Neutralization.—Before this impure alcohol can be refined it must be neutralized with some suitable alkali such as soda ash. The neutralization must be done very carefully since if the solution is boiled when alkaline, the nitrogenous bodies set free amines whose disagreeable odor is hard to remove in the finished alcohol, and which also form blue compounds with copper and color the alcohol. They also tend to combine with the aldehydes forming resins which are likely to gum up the column, or color the alcohol withdrawn from the column yellow. On the other hand, if the solution is acid, esters will form, and any undecomposed ammonium acetate will react with strong alcohol forming ethyl acetate and setting free ammonia.

Intermittent Stills.—Formerly, most alcohol was rectified in intermittent stills. The accompanying table gives the results of a rectification in a modern intermittent still (see Fig. 38). The distillate was divided into the fractions indicated.

Composition of Fractions

		Original liquor	Heads No. 1	Heads No. 2	Last of heads	High-grade alcohol	Trace of tails	Tails No. 2	Tails No. 3	Tails No. 4
Weight	Per cent of original alcohol in each fraction	100.0	1.58	7.53	21.87	26.43	24.90	10.25	4.20	1.20
	Per cent alcohol in fraction	....	92.0	96.1	96.5	96.5	96.4	96.4	93.6	74.0
	Per cent acids (as H Ac)	0.155	0.009	0.0038	0.0038	0.0022	0.0022	0.003	0.007	
Esters		0.074	0.333	0.099	0.017	0.0065	0.011	0.017	0.090	
Aldehydes		0.027	0.58	0.175	0.003	traces	traces	traces	0.010	
Furfurol		0.0002	trace	trace	trace	......	trace	0.0001	0.003	
Higher alcohols		0.42	trace	trace	trace	trace	0.0032	3.13	11.2	
Nitrogen compounds		0.0007	0.0006	0.0003	0.0001	0.00001	0.0001	0.0002	0.002	

It will be noted that the fraction entitled "High-grade Alcohol" comes rather far from being a pure alcohol, and, furthermore, that this fraction contains but 26 per cent of the alcohol in the original liquor. In other words, 74 per cent of the alcohol must be rehandled in order to convert it into high-grade product.

Continuous Stills.—The use of the continuous rectifying still, as developed by Barbet, has enabled alcohol producers to put on the market an alcohol of higher grade than the best produced by the intermittent still without subsequent chemical treatment with charcoal, etc., and to avoid the rehandling of intermediate fraction, at a considerable saving in time, labor, and expense. A simple type of such a still is shown in Fig. 39.

This still consists essentially of a purifying column *C* and a concentrating and exhausting column *D*. The function of the purifying column is to remove the volatile head products, which can be separated from alcohol by fractionation. The function of the concentrating column is to separate the alcohol and water, as well as the impurities which are not removed in the heads.

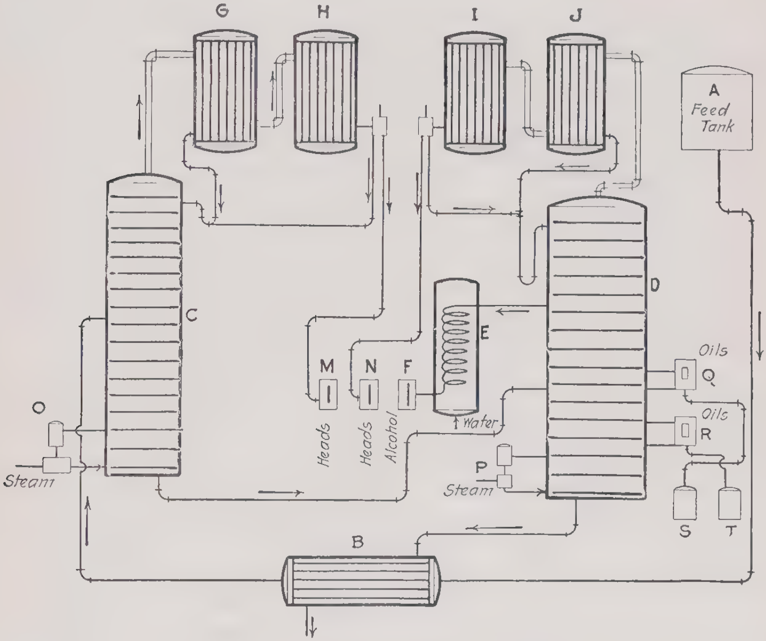


FIG. 39.—Continuous ethyl alcohol still.

The purifying column is fitted with a reflux condenser *G* and condenser *H* and is independent of the rest of the apparatus except that it receives the hot feed continuously from the recuperator *B* and the feed supply tank *A*, and delivers the purified dilute alcohol continuously from its base to the other column *D*. It has its own steam regulator *O* and cooling water supply and its rate of operation can be controlled according to the amount of impurities to be removed.

The operation of the purifying column can be readily understood from the following diagram (Fig. 40) which is credited to Barbet. Ordinates represent the plates in the column, there being 13 plates above the plate on which the feed enters and 10 plates below that point, 24 plates in all. Abscissae below represent per cent alcohol, and above, grams of impurities per hectoliter. The left-hand side of the upper scale is made logarithmic to exaggerate the very low readings while the right-hand side

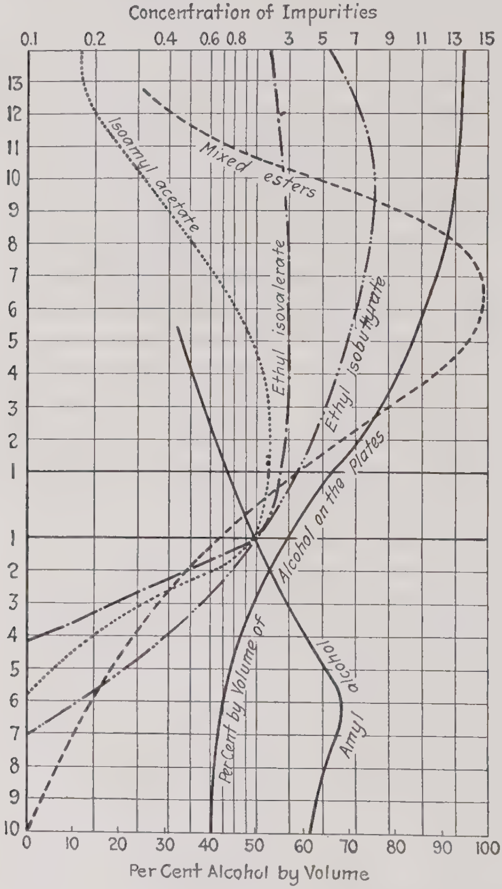


FIG. 40.—Diagram illustrating action of purifying column.

(from 1 to 15) is a normal scale. The lower scale is normal throughout.

The feed consists of a 50 per cent alcohol solution containing heads amounting to 0.5 gram per hectoliter, and higher alcohols (fusel oil) to 2 grams per hectoliter. The mixture distilled from the top of the column is about 95 per cent alcohol, containing 12 grams head products per hectoliter, while the solution discharged from the bottom contains about 40 per cent alcohol, no head products, and 3 grams oils per hectoliter.

The 40 per cent solution then enters the central portion of the column *D*. This column has the reflux condenser *J* and the condenser *I*, and is fitted with a perforated steam pipe and steam regulator *P*, as in the case of the column *C*. This column must remove, as far as possible, the water from the alcohol, and remove the impurities left by the purifying column.

Alcohol and water form a binary mixture of constant boiling point, at a composition of about 96.5 per cent alcohol by weight. This mixture boils about 0.2 degrees below that of pure alcohol, and therefore alcohol can be freed from water only up to that concentration by means of fractional distillation processes.

The impurities left in the alcohol at the entrance to the column *D* consist principally of the higher alcohols, propyl, iso butyl, and iso amyl. These alcohols are completely soluble in ethyl alcohol and can be separated from it by fractional distillation. They are, however, only partly soluble in water, and are therefore volatile with steam when present in excess of their solubility limit. It should be remembered that in the column *D*, the liquid on the top plates is practically pure alcohol in which these oils are soluble, and that the liquid in the bottom of the column is practically all water, in which the oils are practically insoluble. The concentration of alcohol on the intermediate plates varies between these two limits. When the oils are introduced into the column with the dilute alcohol and run down over the plates of the exhausting section of the column, they reach a concentration of alcohol so dilute that they become insoluble and separate out as an oily layer on the plates. The oils are now volatile with steam, and their vapors ascend into the upper portion of the column. Here, however, they are soluble in the higher concentration alcohol and dissolve. But, having a higher boiling

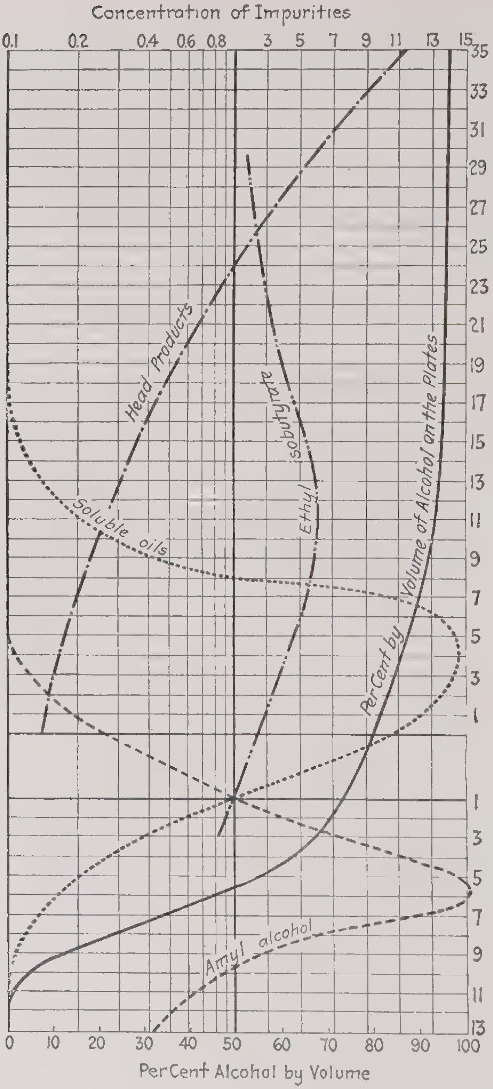


FIG. 41.—Diagram illustrating action of rectifying column.

point than ethyl alcohol, they are forced back down the column. Since they cannot escape either from the bottom or the top of the column, they therefore collect and accumulate in the central portion of it. It is therefore possible by withdrawing the liquid from these plates, where the oils have accumulated, to separate them from the aqueous layers by decantation and return the aqueous alcohol layer to the still. This is the function of the continuous oil decanters *Q* and *R*, which deliver the decanted oil to the tanks *S* and *T* respectively. Since these oils are less soluble the lower the temperature, the liquid withdrawn from the column is sometimes cooled on its way to the decanters by suitable coolers. There are usually two groups of these oils which are of quite different solubility. These collect in two separate portions of the column and must be withdrawn at these separate points, as shown, the oils less soluble in water collecting higher up in the column than those more soluble.

The ethyl alcohol delivered from the top of the column *D* would be freed from all of its impurities other than water, by the removal of the oils, were it not for the fact that during the boiling in the passage through the column, more of the volatile esters are formed, than were removed in the purifying column. These, therefore, tend to accumulate in the top of the column, being more volatile than the alcohol itself. This condition may be shown by another Barbet diagram similar to the one for the purifying column, Fig. 41.

It will be seen from this diagram that the alcohol has reached its maximum strength shortly above the twentieth plate above feed inlet, but that the concentration of heads at that point is only about one-fifteenth that at the top of the column. It is advisable to withdraw the alcohol from the column at this point rather than from the top, and this act is that known as "pasteurization." The heads are distilled out of the column and condensed and delivered to a tester *N* in the same way as the heads from column *C* are delivered to the tester *M*. The hot liquid alcohol withdrawn pasteurized from the column is then cooled in a cooler *E* and delivered to the tester *F*.

The waste liquor from the bottom of the column *D* flows through the recuperator *B* and then to the sewer.

APPENDIX

I. Vapor Pressure Curves for Common Liquids.

II. Vapor Pressure Data of Various Substances arranged according to their Boiling Points at 760 mm. pressure, with references.

III. Boiling Point Relations for Various Binary Mixtures, with references.

IV. Steam Distillation of Various Substances, with references.

V. Heats of Vaporization of Common Substances.

VI. Bibliography (1906–1920).

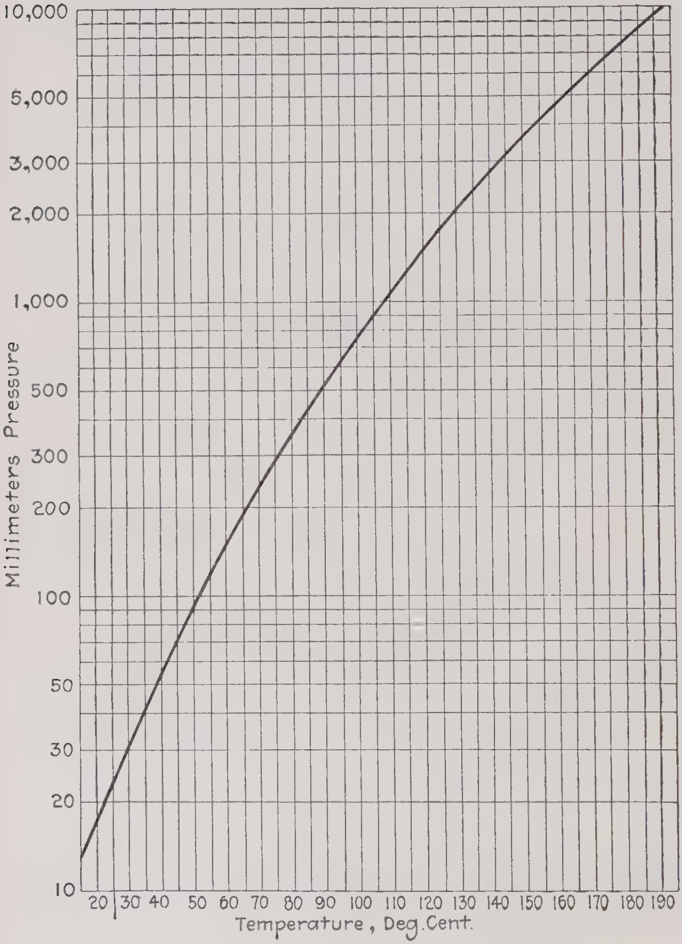


Table I. Fig. 1.—Vapor pressure curve of water.

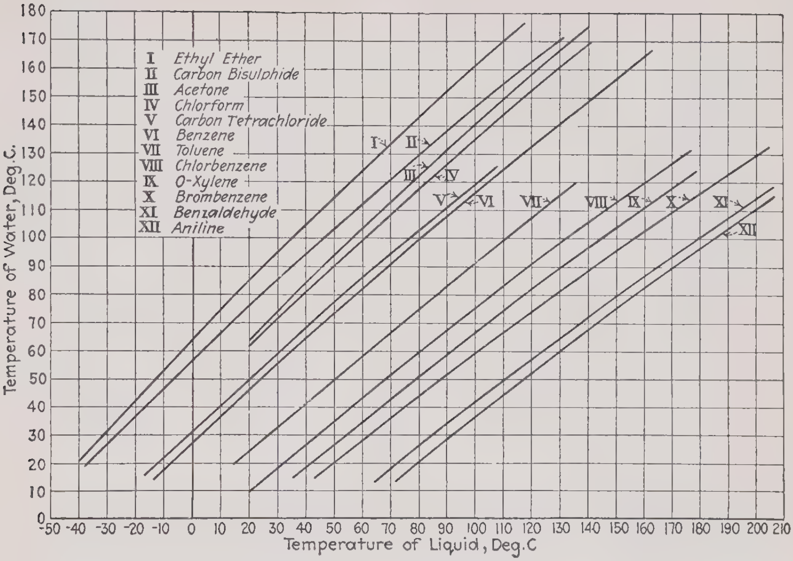


Table I. Fig. 2.—Temperature relations between certain liquids and water at the same pressure. (Explanation: ethyl ether (curve I) at 50°C. has the same vapor pressure as water at 114°C., which by reference to Table I, Fig. 1, is seen to amount to 1300 mm.)

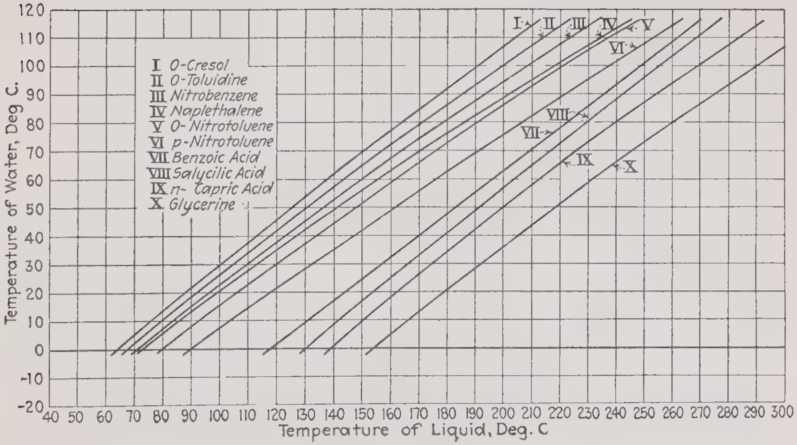


Table I. Fig. 3.

TABLE II.—BOILING TEMPERATURES OF SUBSTANCES AT DIFFERENT PRESSURES, ARRANGED ACCORDING TO THEIR BOILING POINTS AT 760 MM. PRESSURE. TEMPERATURE IN DEGREES CENTIGRADE

This table chiefly from Rechenburg (See Preface)

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures, under lower pressures
	Trimethylamine	$N(CH_3)_3$	9.3°							
	Acetaldehyde	CH_3CHO	20.8							
1	Isopentane	C_5H_{12}	27.95	−20.0	−32.0					
2	Methyl Formate	HCO_2CH_3	31.8	−13.5						
3	Ethyl Ether	$(C_2H_5)_2O$	34.6	−11.1	−24.0					
4	n-Pentane	C_5H_{12}	36.3	−13.2	−26.1					
5	Ethyl Bromide	C_2H_5Br	38.2	−10.4	−23.4					
	Methylal	$CH_2(OCH_3)_2$	41.9							
	Methyl Iodide	CH_3I	42.4							
6	Carbon Bisulphide	CS_2	46.0	− 5.8	−18.0	−23.7	−26.5	−29.4		
124	Cyclopentane	$(CH_2CH_2)_2CH_2$	50.5							
2	Ethyl Formate	$HCO_2C_2H_5$	54.3	+ 5.8	− 7.3					
7	Silicon Tetrachloride	$SiCl_4$	56.9	4.6	− 9	−18.2	−24.8			
7	Acetone	CH_3COCH_3	56.6							
2	Methyl Acetate	$CH_3CO_2CH_3$	57.1	8.9	− 4.5					
	Ethylidene Chloride	CH_3CHCl_2	58.0							
8	Diisopropyl	C_6H_{14}	58.1	4.6	− 8.6					
9	Bromine	Br_2	58.75	8.2	− 5.05	−12.0	−16.65			
10	Chloroform	$CHCl_3$	61.2							
	Dimethyl Acetal	$CH_3CH(OCH_3)_2$	64.4							
12	Methyl Alcohol	CH_3OH	64.7	20.62	+ 8.13	+ 0.16	− 6.81	−16.47	−25.0	
13	n-Hexane	C_6H_{14}	69.0	15.6	+ 1.5	− 7.9	−15.0	−25.7	−34.1	
5	Ethyl Iodide	C_2H_5I	72.3	17.5	3.1					
7	Phosphorus Trichloride	PCl_3	73.8	19.8	4.8					
14	Carbon Tetrachloride	CCl_4	76.8	22.1	7.6	− 2.2	− 9.2	−32.5		
2	Ethyl Acetate	$CH_3CO_2C_2H_5$	77.2	25.9	12.4	+ 3.1	− 3.8	−14.2	−23.9	

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
15	Ethyl Alcohol	C_2H_5OH	78.2	33.9	21.8	12.9	+ 6.3	− 4.3	−14.7	
2	Methyl Propionate	$C_2H_5CO_2CH_3$	79.7	28.1	14.1	4.8	− 1.8	−12.6	−22.3	
14	Benzene	C_6H_6	80.2	25.8	11.6	1.8	− 4.3	−13.6	−22.1	
16	Hexamethylene	C_6H_{12}	80.9	25.2	11.0	1.3				
2	Propyl Formate	$HCO_2C_3H_7$	80.9	29.0	14.7	5.2	− 1.4	−12.6	−23.0	
10	Ethylene Chloride	CH_2ClCH_2Cl	83.5							
17	Fluorbenzene	C_6H_5F	84.9	30.8	16.0	6.0	− 1.0	−13.0		
18	Methyl Isopropyl Ketone	$CH_3COC_3H_7$	88.9		32.1	23.2	+17.9	+11.9		
2	Methyl Isobutyrate	$C_3H_7CO_2CH_3$	92.3	38.8	24.2	14.6	7.7	− 3.6	−13.8	
	Propionitril	CH_3CN_2CN	95.9							
19	n-Propyl Alcohol	C_3H_7OH	97.4	51.8	39.5	30.8	23.9	+13.2	+ 3.5	
20	Chloral Hydrate	$CCl_3CHO.H_2O$	97.5	53.2	48.3	36.0	28.2	18.2		
20	Chloral	CCl_3CHO	97.7	40.4	23.7	16.0				
21	Isobutyl Formate	$HCO_2C_4H_9$	97.9	42.9	28.4	19.0				
22	n-Heptane	C_7H_{16}	98.4	41.6	26.4	16.3	9.5	− 2.1		
145	Heptylene	C_7H_{14}	98.5							
2	Ethyl Propionate	$C_2H_5CO_2C_2H_5$	99.0	44.9	30.8	21.1	13.6	+ 2.1	− 7.8	
	Water	H_2O	100.0	51.7	38.3	29.9	22.3	11.4	+1.3	
23	Formic Acid	HCO_2H	100.8	46.9	31.0	19.5	12.3	− 0.3		
2	Propyl Acetate	$CH_3CO_2C_3H_7$	101.6	47.1	32.6	22.8	15.4	+ 4.4		
18	Diethyl Acetate	$CH_3CH(OC_2H_5)_2$	102.2	47.3	32.8	25.0	20.2			
2	Methyl Butyrate	$C_3H_7CO_2CH_3$	102.8	48.0	33.0	23.2	15.6	4.2	− 6.1	
24	Dimethyl Ethyl Carbinol	$(CH_3)_2C_2H_5COH$	102.9					19.0		
	Methyl Propyl Ketone	$CH_3COC_3H_7$	103.3							
25	Chloral-Methyl Alcohol	$CCl_3CHO.CH_3OH$	106.0							
18	Piperidine	$CH_2(CH_2CH_2)_2NH$	106.0	42.2	30.4	22.1	17.2			
26	Formic Acid-Hydrate	$HCO_2H.H_2O$	107.6							
27	Isobutyl Alcohol	C_4H_9OH	107.9	61.7	47.3	40.2	33.9	21.2	11.1	
8	Diisobutyl	C_8H_{18}	109.2	50.8	34.9	24.5	16.9	5.7	− 6.0	
21	Ethyl Isobutyrate	$C_3H_7CO_2C_2H_5$	110.1	53.6	38.2					
28	Toluene	$C_6H_5CH_3$	110.4	51.8	36.3	25.5	17.9	6.0		
29	Tin Chloride	$SnCl_4$	114.2	55.35	39.6	29.9	21.1	8.8?	− 3.2	
28	Pyridine	C_5H_5N	114.5	51.9	41.6	34.0	27.0	18.3		
10	Nitro Ethane	$C_2H_5NO_2$	114.9							
21	Isobutyl Acetate	$CH_3CO_2C_4H_9$	116.3	59.7	43.7					
21	Methyl Valerianate	$C_4H_9CO_2CH_3$	116.7	59.4	45.4					

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
28	n-Butyl Alcohol	C_4H_9OH	117.6	69.8	56.9	48.0	41.5	31.0	21.7	
18	Isoamyl Bromide	$(CH_3)_2CH\ CH_2\ CH_2\ Br$	118.6		43.5	33.4	27.0	17.6		
9	Acetic Acid	CH_3CO_2H	118.7	63.1	47.0	36.6	29.3	16.8	5.5	0° 3.3
21	Ethyl Butyrate	$C_3H_7CO_2C_2H_5$	119.9	62.6	46.1					
24	Isobutyl Iodide	C_4H_9I	120.0				30.0	17.0		
32	Isopropyl Isobutyrate	$C_3H_7CO_2C_3H_7$	120.2	62.3	46.8	36.4	29.0	16.4	7.0	
21	Propyl Propionate	$C_2H_5CO_2C_3H_7$	122.2	65.1	48.0					
24	Caprylene (Oxtylene)	C_8H_{16}	123.0				31.0	19.0		
10	Paraldehyde	$(CH_3CHO)_3$	123.1							
21	Amyl Formate	$HCO_2C_5H_{11}$	123.3	65.4	47.8	39.2	29.2	18.6		
33	n-Octane	C_8H_{18}	125.8	65.6	50.2	39.3	31.3	19.1	7.7	0° 2.94
18	Picoline	$CH_3C_5H_4N$	126.2		57.3	45.1	37.4	24.4		
18	Mesityl Oxide	$(CH_3)_2C\ CH\ CO\ CH_3$	129.5		55.0		37.9	26.5	18.5	
34	Isoamyl Alcohol	$C_5H_{11}OH$	130.1	80.7	66.9	58.4	51.5	40.3	30.2	10° 1
5, 10	Ethylen Bromide	$CH_2Br\ CH_2Br$	131.5	70.4	53.1	41.6	32.7	18.6	4.4	−20° 1.73
17	Chlorbenzene	C_6H_5Cl	131.8	70.4	53.7	42.7	34.5	21.8	10.4	0° 2.56
21	Propyl Isobutyrate	$C_3H_7CO_2C_3H_7$	133.9	73.9	58.7	48.5				
21	Ethyl Valerianate	$C_4H_9CO_2C_2H_5$	134.3	74.4	61.0	51.0				
18	Acetic Anhydride	$(CH_3CO)_2O$	136.4	104.0?	66.4	55.6	49.2	39.9		
35	Ethyl Benzene	$C_6H_5C_2H_5$	136.6	74.2	57.4	46.2		30.0		
21	Isobutyl Propionate	$C_2H_5CO_2C_4H_9$	136.8	77.8	65.3					
24	Allyl Sulphide	$(C_3H_5)_2S$	138.6				41.0	28.0		
35	p-Xylene	$C_6H_4(CH_3)_2$	138.9	76.4	59.5	48.0				
146	Pentamethylen Alcohol	$(CH_2CH_2)_2CH\ OH$	139.0							
35	m-Xylene	$C_6H_4(CH_3)_2$	139.2	76.9	60.2	49.1		30.0		
24	Diisobutyl Amine	$(C_4H_9)_2NH$	139.5				43.0	31.0		
34, 36	Propionic Acid	$C_2H_5CO_2H$	140.3	87.6	71.9	60.4	53.1	42.1	29.5	20° 3.0 10° 1.5
28	Propylen Bromide	$CH_3CH\ Br\ CH_2Br$	141.0	78.4	61.8	50.6	42.5	29.0		

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
21	Propyl Butyrate	$C_3H_7CO_2C_3H_7$	142.7	81.9	65.4	55.0				
35	o-Xylene	$C_6H_4(CH_3)_2$	144.0	81.2	64.1	52.6	44.5			
37	Styrol	$C_6H_5CH\ CH_2$	145.5				49.0	36.0		
21	Isobutyl Isobutyrate	$C_3H_7CO_2C_4H_9$	146.6	85.8	68.2	56.0				
24	Amyl Nitrate	$NO_3C_5H_{11}$	147.5					40.0		
24	Amyl Iodide	$C_5H_{11}I$	148.2					35.0		
18	Allyl Mustard Oil	C_3H_5NCS	148.2	91.0	72.2	60.7	53.8	41.5		
38	n-Nonane	C_9H_{20}	149.5	86.0	70.0	59.0	49.0	38.0		
18	Bromoform	$CH\ Br_3$	150.5		66.0	56.7	49.9	40.9		
39	Methyl-n-Amyl Ketone	$CH_3CO\ C_5H_{11}$	151.0							
34	Isobutyric Acid	$C_3H_7CO_2H$	153.3	97.6	82.2	71.4	63.2	51.0	38.8	20° 1.5 10° 0.7
147	Trimethylamine-Acetate	$(CH_3)_3N.4CH_3CO_2H$	154.3			76–77				
28	n-Heptyl Aldehyde	$CH_3(CH_2)_5CHO$	155.0	82.4	70.2	61.9	54.2	45.3		
35	Isopropyl Benzene	$C_6H_5CH(CH_3)_2$	155.1	90.1	72.5	60.8	52.0			
28	Brombenzene	C_6H_5Br	155.5	90.0	73.0	61.2	52.8	40.6	29.8	22.3_3° 10.9_1°
24	Phenyl Methyl Ether (Anisol)	$C_6H_5OCH_3$	155.5					42.5		
21	Propyl Valerianate	$C_4H_9CO_2C_3H_7$	155.9	93.9	79.5					
5	Pinene	$C_{10}H_{16}$	156.0	92.0	79.0	63.0	53.0	38.0	22.0	
21	Isobutyl Butyrate	$C_3H_7CO_2C_4H_9$	156.9	94.7	76.3					
	n-Hexyl Alcohol	$C_6H_{14}O$	157.0							
24	n-Propyl Benzene	$C_6H_5C_3H_7$	158.8				57.0	45.0		
21	Amyl Propionate	$C_2H_5CO_2C_5H_{11}$	160.2	97.4	80.4	70.0	59.4	45.9	29.3	
40	Camphene	$C_{10}H_{16}$	160.5				62.0	46.0		
18	p-Chlor Toluene	$C_6H_4ClCH_3$	161.5		77.7	66.5	59.6	48.9		
148	Furfurol	$\left\{\begin{matrix}CH\ C\ (CHO)\\ CH\ CH\end{matrix}\right\}O$	161.5							
24	p-Ethyl Toluene	$C_6H_4\ (C_2H_5)CH_3$	162.0					46.0		
34	n-Butyric Acid	$C_3H_7CO_2H$	162.2	106.4	90.9	80.3	72.0	59.6	47.4	40° 3.0 30° 1.5 20° 0.76

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
24	Tribrom Ethylene	$CH\ Br\ CBr_2$	162.5							
41	Methyl Oxalate	$(CO_2CH_3)_2$	164.0							
28	Trimethylen Bromide	$CH_2BrCH_2CH_2Br$	164.4	99.4	82.0	70.4	61.6	48.0		
24	Mesitylene	$C_6H_3(CH_3)_3$	164.5					49.0		
18	Propionic Acid Anhydride	$(C_2H_5CO)_2O$	167.0		86.7	77.4	70.4	59.0		
21	Isobutyl Valerianate	$C_4H_9CO_2C_4H_9$	168.7	104.8	85.3	76.0				
21	Amyl Isobutyrate	$C_3H_7CO_2C_5H_{11}$	168.8	104.4	86.3	76.0				
	n-Hexyl Acetate	$CH_3CO_2C_6H_{13}$	169.0							
149	Ethyl-n-Amyl Ketone	$C_2H_5CO\ C_5H_{11}$	170.0							
42	Furfuralcohol	$C_4H_3OCH_2OH$	171.0				81.0	68.0		
24	Methyl Hexyl Ketone	$CH_3CO\ C_6H_{13}$	171.0					60.0		
43	Myrcene	$C_{10}H_{16}$	171.5				67.0			
24	Isocrotonic Acid	$C_3H_5CO_2H$	171.9					69.0		
44	Phenetol	$C_6H_5O\ C_2H_5$	172.0		87.7	76.4	70.0	59.0		
45	Decylene	$CH_2CH\ (CH_2)_7CH_3$	172.0	107.0	88.0		68.0	54.0		
24	Amyl Ether	$(C_5H_{11})_2O$	172.5					56.0		
38	n-Decane	$C_{10}H_{22}$	173.0	107.0	90.0	78.0	68.0	55.0		
	Methyl Heptenone	$(CH_3)_2CCH\ CH_2$- CH_2CH_3CO	173.0							
18	Bromal	$C\ Br_3CHO$	174.0	110.1	92.4	80.7	74.1	62.3		
28	p-Cymole	$C_6H_4(C_3H_7)\ CH_3$	174.3					57.0		
34	Isovalerianic Acid	$C_4H_9CO_2H$	174.7	118.2	102.5	91.6	83.3	70.9	58.7	40° 1.5 20° 0.37
	Sylvestrene	$C_{10}H_{16}$	175.0							
47	Phellandrene	$C_{10}H_{16}$	175.0					α59.0 β55.0	47.0	
40	n-Octyl Aldehyde	$C_7H_{15}CHO$	175.0					61.0		
24	d-Limonene	$C_{10}H_{16}$	175.0					54.0		
24	Amylen Bromide	$C_5H_{10}Br_2$	175.0				71.0	58.0		
49	Methyl Heptenol	$(CH_3)_2C\ CH\ CH_2$- $CH_2CH(CH_3)OH$	175–176						65.0	
24	d-Heptyl Alcohol	$C_7H_{15}OH$	175.8				86.0	73.0		
48	Cineol	$C_{10}H_{18}O$	176.0				66.0	54.0		
28	Benzaldehyde	C_6H_5CHO	178.3	112.5	95.3	83.5	75.2	62.0	50.1	42.5° 3 29.3° 1

TABLE II.—*Continued*

Lit. Ref	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
18	Octyl Alcohol	$CH_3(CH_2)_5CH(OH)CH_3$	178.5	106.0	94.4	86.6	82.3	75.4		
21	Amyl Butyrate	$C_3H_7CO_2C_5H_{11}$	178.6	113.1	94.2	84.0				
18	Benzyl Chloride	$C_6H_5CH_2Cl$	179.0		94.5			66.1		
147	Trimethylamin-Formate	$2(CH_3)_3N.5HCO_2H$	179–180.5				100.3	87.7		
150	Octyl Chloride	$C_8H_{17}Cl$	180.0							
18	Aceto-Acetic Ester	$CH_3CO\ CH_2C_2H_5$	180.8		95.5	88.0	80.3	67.2		
28	Phenol	C_6H_5OH	181.4	120.2	104.7	93.8	85.8	73.5	62.5	55.8° 3 44.8° 1
18	α-Dichlorhydrine	$CH_2ClCH(OH)CH_2Cl$	182.0		95.1	85.6	79.1	68.8		
18	o-Brom Toluene	$C_6H_4BrCH_3$	183.0		95.7	83.0	75.2	63.4		
24	Benzyl Amine	$C_6H_5CH_2NH_2$	183.0				80.0	68.0		
28	Aniline	$C_6H_5NH_2$	183.9	119.4	101.9	90.9	82.8	69.2	57.9	51.8° 3 43.1° 1
28	n-Valerianic Acid	$C_4H_9CO_2H$	184.4	128.3	112.1	100.7	93.0	80.8	70.5	65° 3.1 55° 1.0 45° 0.1
28	Dimethyl-o-Toluidine	$C_6H_4(CH_3)N(CH_3)_2$	184.8	118.1	100.4	88.5	79.7	66.2	54.1	
24	Benzyl Ethyl Ether	$C_6H_5CH_2OC_2H_5$	185.0					65.0		
24	Crotonic Acid	$C_3H_5CO_2H$	185.0				93.0	80.0		
50	Iodine	I_2	185.3	117.0	102.15	92.2	85.0	72.4	61.0	
18	Ethyl Oxalate	$(CO_2C_2H_5)_2$	185.3		113.2	103.3	96.5	83.9		
145	Heptyl Iodide	$C_7H_{15}I$			98.0					
40	Terpinolene	$C_{10}H_{16}$	186.0				87.0	69.0		
151	Pentanonal	$CH_3CO\ CH_2CH_2CHO$	186–188					68.0		
17	Iodo Benzene	C_6H_5I	188.2	118.1	99.7	87.0	78.0	63.3	50.5	40° 2.73 30° 1.48
28	Monochlor Acetic Acid	CH_2ClCO_2H	188.9	132.0	115.0	104.6	96.9	84.7	71.4	

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
28	o-Cresol	$C_6H_4(CH_3)OH$	190.1	127.4	110.3	98.8	90.6	77.6	65.5	36.6° 1
28	Benzonitril	C_6H_5CN	190.6	121.3	103.9	92.1	83.0	69.1	56.9	50.0° 3 38.4° 1
150	n-Octyl Alcohol	$CH_3(CH_2)_6CH_2OH$	190-192							
51	n-Nonyl Aldehyde	$CH_3(CH_2)_7CHO$					85.0	72.0		
52	Fenchone	$C_{10}H_{16}O$	191.0				83.0	69.0		
28	Dimethyl Aniline	$C_6H_5N(CH_3)_2$	193.1	125.7	108.2	96.3	87.5	73.1	61.6	41.1° 1
28	Methyl Aniline	$C_6H_5NH\ CH_3$	193.8	129.8	112.5	101.1	92.6	79.2	67.7	46.8° 1
18	Isoamyl Isovalerianate	$C_4H_9CO_2C_5H_{11}$	194.0		102.8	93.4	86.6	71.0		
38	n-Undecane	$C_{11}H_{24}$	194.5	127.0	108.5	96.5	87.0	72.0		
53	Methyl Heptyl Ketone	$CH_3CO\ C_7H_{15}$	195.0				86.0	74.0		
	Methyl Octyl Ketone	$C_5H_{11}CH(CH_3)CH_2\text{-}CO\ CH_3$	196–198							
24	Salicylic Aldehyde	$C_6H_4(OH)\ CHO$	197.0							
153	Androl	$C_{10}H_{20}O$	197–198					74.0		
28	Benzoyl Chloride	$C_6H_5CO\ Cl$	197.1	128.0	109.4	97.2	88.2	73.8	60.5	38.6° 1
54	Ethylen Glykol	$C_2H_4(OH)_2$	197.1	140.6	124.7			89.0		
28	Methyl Benzoate	$C_6H_5CO_2CH_3$	197.5	130.8	112.6	100.5	91.6	77.3	64.4	43.0° 1
40	Linalool	$C_{10}H_{18}O$	198.0			101.0	93.0	81.0	68.0	
150	Octyl Bromide	$C_8H_{17}Br$	198–200							
24	Formamide	$H\ CO\ NH_2$								
154	Methyl-n-Heptyl Carbinol	$CH_3(CH_2)_6CHOH\ CH_3$	198 200					97.0		
28	o-Toluidine	$C_6H_4CH_3NH_2$	199.7	133.0	115.1	103.6	94.9	81.4	69.3	61.4° 3 46.2° 1
28	p-Toluidine	$C_6H_4(CH_3)NH_2$	200.4	133.7	115.8	104.3	95.6	82.3	70.1	46.9° 1
28	m-Cresol	$C_6H_4(CH_3)OH$	200.5	138.0	120.8	109.5	101.3	87.8	76.0	55.9° 1

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
28	Isocapronic Acid	$(CH_3)_2CH(CH_2)_2$-CO_2H	200.5	141.3	125.3	114.9	106.8	93.9	82.0	70° 1.5 60° 0.3
35	Thujone	$C_{10}H_{16}O$	201.0				93.0	80.0		
28	p-Cresol	$C_6H_4(CH_3)OH$	201.1	138.4	121.3	110.1	101.8	88.6	76.5	55.7° 1
28	Acetophenone	$C_6H_5CO\ CH_3$	201.5	133.2	114.7	102.4	93.4	79.0	65.0	
155	Isopulegone	$C_{10}H_{16}O$						87.0		
156	Isopulegol	$C_{10}H_{18}O$						87.0		
28	m-Toluidine	$C_6H_4(CH_3)NH_2$	203.3	136.6	118.7	107.1	98.5	85.3	72.8	49.8° 1
28	Ethyl Aniline	$C_6H_5NH\ C_2H_5$	204.0	136.8	119.1	106.7	97.6	83.8	72.0	49.0° 1
	Benzyl Formate	$HCO_2CH_2C_6H_5$	204.0							
150	Ethyl-n-caprylate	$C_7H_{15}CO_2C_2H_5$	204–206							
56	Citronellal	$C_{10}H_{18}O$	205.0			106.0	96.0	84.0		
58	Camphene Hydrate	$C_{10}H_{16}.H_2O$	205.0							
57	n-Hexyl-n-Butyrate	$C_3H_7CO_2C_6H_{13}$	205.0							
28	Benzyl Alcohol	$C_6H_5CH_2OH$	205.0	141.3	124.4	113.4	105.3	92.6	80.8	72.9° 3 60.9° 1
24	Guaiacol	$C_6H_4(OCH_3)OH$	205.1					92.0		
28	n-Capronic Acid	$C_5H_{11}CO_2H$	205.7	146.0	129.9	119.2	111.1	99.0	90.4	80° 2.5 70° 0.9
59	Camphor	$C_{10}H_{16}O$	206.0	138.7	118.8	104.0	95.8	82.6	71.1	65° 3.4 55° 1.85 45° 0.90
10	Menthone	$C_{10}H_{18}O$	207.0							
60	n-Decyl Aldehyde	$CH_3(CH_2)_8CHO$	208.0					92.0		
61	Dodecylene	$CH_2CH(CH_2)_9CH_3$	208.0				102.0	89.0		

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
28	Nitrobenzene	$C_6H_5(NO_2)$	208.3	139.9	120.2	108.2	99.1	85.4	72.9	64.9° 3 53.1° 1
28	o-Chloraniline	$C_6H_4CNH_2$	208.8	139.5	120.7	108.4	99.2	84.8	72.3	
28	Dimethyl-p-Toluidine	$C_6H_4(CH_3)N(CH_3)_2$	209.5	140.3	121.8	109.3	100.4	86.7	74.3	
62	Terpineol (Melting point 32–33°)	$C_{10}H_{18}O$	209.5					90		
38	n-Methyl Octyl Ketone	$C_8H_{17}CO\ CH_3$	211.0	142.0						
18	m-Xylidine	$C_6H_3(CH_3)_2NH_2$	211.5		125.8	114.2	107.6	93.0		
	Borneol	$C_{10}H_{18}O$	212.0							
24	Propionamide	$C_2H_5CO\ NH_2$	213.0				119.0	104.0		
154	Methyl-Heptyl Carbinol Acetate	$CH_3CO_2C_9H_{19}$	213–215							
24	Ethyl Benzoate	$C_6H_5CO_2C_2H_5$	213.4					86.0		
63	n-Nonyl Alcohol	$C_9H_{19}OH$	213.5				114.0	99.0		
64	Menthol	$C_{10}H_{20}O$	213.6					96.0		
40	Bornyl Formate	$HCO_2C_{10}H_{17}$	about 214.0				104.0	90.0		
38	n-Dodecane	$C_{12}H_{26}$	214.5	145.5	126.0	113.8	103.0	88.0		
65	Methyl Chavicol	$C_6H_4(OCH_3)C_3H_5$	215.0					93.0	81.0	
24	Dimethyl Resorcine	$C_6H_4(OCH_3)_2$	215.0				104.0	92.0		
158	1.3-Dimethyl Benzaldehyde 4.	$(CH_3)_2C_6H_3CHO$	215–216					99.0		
28	Diethyl Aniline	$C_6H_5N(C_2H_5)_2$	215.5	147.3	128.6	116.4	107.2	91.9	79.3	
66	Benzyl Acetate	$CH_3CO_2CH_2C_6H_5$	216.0							
72	Phenyl Ethyl Alcohol	$C_6H_5CH_2CH_2OH$	218–220					101.0		
67	Naphthaline	$C_{10}H_8$	218.1		125.8	112.6	101.9	86.9	75.0	70° 2.92 65° 1.92 60° 1.24
18	Phenyl Mustard Oil	C_6H_5NCS	218.5		126.6	114.6	106.2	91.2		
68	Terpineol (Melting Point 35–36°)	$C_{10}H_{18}O$	219.0				110.0	98.0		
69	Menthyl Formate	$HCO_2C_{10}H_{19}$	219.0					90.0		
159	Tert. Butyl Phenyl Ketone	$C_6H_5CO\ C(CH_3)_3$	219–221					99.0		
40	Linalyl Acetate	$CH_3CO_2C_{10}H_{17}$	220.0			120.0	112.0	96.0		
28	o-Nitrotoluene	$C_6H_4(CH_3)NO_2$	220.4	150.6	131.7	119.2	109.6	94.8	81.8	

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
40	Pulegone	$C_{10}H_{16}O$	221.0		126.0		106.0	94.0		
	Pulegol	$C_{10}H_{18}O$					111.0	98.0		
160	Dihydro Citronellol	$C_{10}H_{22}O$					114–116	102–104		
28	n-Heptylic Acid	$C_6H_{13}CO_2H$	221.0	160.0	144.0	132.9	125.1	113.2	105.5	90° 1.9 80° 0.7
70	Dihydro Carveol	$C_{10}H_{18}O$	222.0				118.0	105.0	94.0	
24	Acetamide	$CH_3CO\ NH_2$	222.0					105.0		
71	Diacetamide	$(CH_3CO)_2NH$	223.0					108.0		
40	Dihydro Carvone	$C_{10}H_{16}O$	223.0				106.0			
40	Bornyl Acetate	$CH_3CO_2C_{10}H_{17}$	223.0				113.0	98.0		
73	Methyl Salicylate	$C_6H_4(OH)CO_2CH_3$	223.0					95.0		
74	n-Octyl Iodide	$C_8H_{17}I$	225.5				106.5	90.5		
40	Citronellol	$C_{10}H_{20}O$	226.0				122.0	111.0	99.0	
161	Nerole	$C_{10}H_{18}O$	226–227			128.7	120.3			
40	Menthyl Acetate	$CH_3CO_2C_{10}H_{19}$	227.0				114.0	102.0		
161	Neryl Formate	$HCO_2C_{10}H_{17}$				123–125	114–116			
40	Citral	$C_{10}H_{16}O$	228.0				118.0	106.0		
28	m-Chloraniline	$C_6H_4Cl\ NH_2$	228.5	158.0	138.8	126.2	116.8	102.0	89.8	
24	n-Propyl Benzoate	$C_6H_5CO_2C_3H_7$	229.5					98.0		
163	Citronellal Dimethyl Acetal	$C_{10}H_{18}(OCH_3)_2$						106–107		
164	Citronellyl Formate	$HCO_2C_{10}H_{19}$						97–100		
75	Carvone	$C_{10}H_{14}O$	230.0		137.0	125.0		102.0	90.0	34.5° 0.192 22.6° 0.069
40	Geraniol	$C_{10}H_{18}O$	230.0				124.0	110.0	101.0	
76	Methyl-n-Nonyl Ketone	$CH_3CO\ C_9H_{19}$	231.0				120.0	108.0	95.0	
74	n-Decyl Alcohol	$C_{10}H_{21}OH$	231.0				125.0	112.0		
154	Methyl-n-Nonyl Carbinol	$CH_3(CH_2)_8CH\ OH$ CH_3	231–233				126.0	115.0		
18	Ethyl Salicylate	$C_6H_4(OH)CO_2C_2H_5$	231.5		139.1	127.1	119.0	104.8		
77	Thymol	$C_6H_3(CH_3)(C_3H_7)OH$	231.8					109.0		
	Thymochinone	$C_{10}H_{12}O_2$	232.0							
40	Diosphenol (Buccocamphor)	$C_{10}H_{16}O_2$	232.0					109.0		
28	Cumine Aldehyde	$C_6H_4(C_3H_7)CHO$	232.0	158.0	138.1	125.5	117.9	103.5	91.0	
40	Safrol	$C_6H_3(O_2CH_2)C_3H_5$	233.0				123.0	107.0	93.0	

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
	Isobutyl Oxalate	$(CO_2C_4H_9)_2$	233.0					106.0		
24	Heptyl Benzene	$C_6H_5C_7H_{15}$	233.0					108.0		
165	Phenyl Acetic Nitril	$C_6H_5CH_2CN$	233.5							
38	n-Tridecane	$C_{13}H_{28}$	234.0	162.5	142.5	130.0	120.0	106.0		
24	Pseudo Cumidine	$C_6H_2(CH_3)_3NH_2$	234.5					109.0		
40	Bornyl Propionate	$C_2H_5CO_2C_{10}H_{17}$	235.0				123.0	108.0		
24	Anethol	$C_6H_4(OCH_3)C_3H_5$	235.0					106.0		
78	Phenyl Propyl Alcohol	$C_6H_5(CN_2)_2CH_2OH$	235.0					116.0		
166	Geranyl Formate	$HCO_2C_{10}H_{17}$					118–119	102–103		
161	Neryl Acetate	$CH_3CO_2C_{10}H_{17}$					137.5	129.5		
79	Carvacrol	$C_6H_3(CH_3)(C_3H_7)OH$	237.0					113.0		
24	p-Isobutyl Phenol	$C_6H_4(C_4H_9)OH$	237.0					116.0		
80	Chavicol	$C_6H_4(OH)C_3H_5$	237.0							
18	Isobutyl Benzoate	$C_6H_5CO_2C_4H_9$	237.0		146.0	133.0	124.4	109.5		
28	n-Caprylic Acid	$C_7H_{15}CO_2H$	237.5	174.0	156.4	144.9	136.6	124.6	113.7	105° 2.6 95° 0.8
28	p-Nitro Toluene	$C_6H_4(CH_3)NO_2$	237.7	164.0	143.8	130.4	120.3	105.6	92.3	
81	Chinoline	C_9H_7N	237.8	166.7	142.3	129.0	119.0	103.0	89.0	
167	Ethyl-p-Tolyl Ketone	$CH_3C_6H_4CO\ C_2H_5$	238–239			129.0	121.5			
69	Menthyl Propionate	$C_2H_5CO_2C_{10}H_{19}$						110.0		
82	Linalyl Propionate	$C_2H_5CO_2C_{10}H_{17}$						115.0		
84	Citronellyl Acetate	$CH_3CO_2C_{10}H_{19}$					126.0	113.0		
85	Bornyl Isobutyrate	$C_3H_7CO_2C_{10}H_{17}$	243.0							
	Benzyl Mustard Oil	$C_6H_5CH_2NCS$	243.0							
69	Menthyl n-Butyrate	$C_3H_7CO_2C_{10}H_{19}$						121.0		
86	Tetradecylene	$CH_2CH(CH_2)_{11}CH_3$	243.0				133.0	120.0		
87	n-Octyl-n-Butyrate	$C_3H_7CO_2C_8H_{17}$	244.0							
74	n-Nonyl Iodide	$C_9H_{19}I$					123.0	109.0		
154	Methyl-n-Nonyl Carbinol Acetate	$CH_3CO_2C_{11}H_{23}$	245.0							
88	Geranyl Acetate	$CH_3CO_2C_{10}H_{17}$	245.0				133.0	119.0		
24	Pyrocatechinol	$C_6H_4(OH)_2$	245.5					119.0		
	n-Hexyl Capronate	$C_5H_{11}CO_2C_6H_{13}$	246.0							
38	Methyl Decyl Ketone	$C_{10}H_{21}CO\ CH_3$	246.5	177.5						
24	Chinaldine	$C_{10}H_9N$	246–247					118.0		
24	Cumine Alcohol	$C_6H_4(C_3H_7)CH_2OH$	246.6					127.0		

TABLE II.—*Continued*

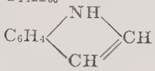
Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
40	Bornyl-n-Butyrate	$C_3H_7CO_2C_{10}H_{17}$	247.0				133.0	120.0		
	Methyl Pseudo Cumyl Ketone	$(CH_3)_3C_6H_2CO\ CH_3$	247–248				137–138			
90	Methyl Eugenol	$C_6H_3(OCH_3)_2C_3H_5$	248.0					127.0		
91	Anisaldehyde	$C_6H_4(OCH_3)CHO$	248.0					118.0?	94.0	
92	Dodecyl Amine	$C_{12}H_{25}NH_2$	248.0				140.0	125.0		
93	Benzoic Acid	$C_6H_5CO_2H$	249.0	185.9	167.2	155.5	146.5	132.5	116.2	110° 3.74 100° 1.40 90° 0.60 80° 0.30 70° 0.16 60° 0.11
168	Octyl Valerianate	$C_4H_9CO_2C_8H_{17}$	249–251							
94	Ionone	$C_{13}H_{20}O$	250.0					123.0		
95	Eugenol	$C_6H_3(C_3H_5)(OCH_3)$-OH	about 250.5			146.0		125.0		
24	n-Propyl Succinate	$(CH_2CO_2C_3H_7)_2$	250.8					123.0		
96	Geranyl Isobutyrate	$C_3H_7CO_2C_{10}H_{17}$	251.0					133.0		
38	n-Tetradecane	$C_{14}H_{30}$	about 252.5	178.5	158.0	145.5	136.0	121.0		
	Indol		253–254							
28	n-Pelargonic Acid	$C_8H_{17}CO_2H$	253.4	188.0	170.3	159.0	150.0	136.9	126.6	120° 3 110° 1.2 100° 0.3
100	Isosafrol	$C_6H_3(O_2CH)_2)C_3H_5$	254.0						107.5	
24	Styrol Dibromide	$C_6H_5CH\ Br\ CH_2Br$	254.0					129.0		

TABLE II.—*Continued*

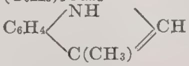
Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressure
97	Diphenyl	$(C_6H_5)_2$	254.0					117.0		
95	Betolphenol	$CH_3(C_3H_5)(OH)$-OCH_3	254.0					127.0		
45	Decylene Gycol	$C_{10}H_{20}(OH)_2$	255.0				151.0	137.0		
98	Bornyl Isovalerianate	$C_4H_9CO_2C_{10}H_{17}$						138.0		
99	Salicylic Acid	$C_6H_4(OH)CO_2H$	256.0	193.4	177.2	164.7	156.2	143.9	135.5	
169	Citronellic Acid	$C_{10}H_{18}O_2$	about 257.0				154.0	143.5		
100	Methyl Cinnamate	$C_6H_5(CH)_2CO_2CH_3$	258.0					123.0		
28	α-Chlornaphthaline	$C_{10}H_7Cl$	259.3	180.4	159.3	145.1	134.7	118.6	104.8	80.6° 1
96	Geranyl-n-Butyrate	$C_3H_7CO_2C_{10}H_{17}$						139.0		
45	Decylene Dibromide	$C_{10}H_{20}Br_2$					151.0	137.0		
40	Caryophyllene	$C_{15}H_{24}$	260.0					120.0		
74	n-Decyl Iodide	$C_{10}H_{21}I$					138.0	124.0		
101	Succinic Acid Anhydride	$(CH_2CO)_2O$	261.0	189.0	169.0		145.0	130.0		
40	Isoeugenol	$C_6H_3(C_3H_5)(OCH_3)$-OH	261.0	193.0			150.0		117.0	
170	Lauric Aldehyde	$C_{12}H_{24}O$		184–185						
171	Geranialic Acid	$C_{10}H_{16}O_2$						147.5		
172	Phenyl Propionic Nitril	$C_6H_5(CH_2)_2CN$	261.0							
18	Isoamyl Benzoate	$C_6H_5CO_2C_5H_{11}$	262.0		165.8	148.2	138.4	124.8		
38	Methyl Undecyl Ketone	$C_{11}H_{23}CO\ CH_3$	262.5	191.5						
24	Piperonal	$C_6H_3(O_2CH_2)CHO$	263.0				149.0	135.0		
102	Methyl Isoeugenol	$C_6H_3(OCH_3)_2C_3H_5$	263.0							
	Cedrene	$C_{15}H_{24}$	263.0							
	β-Santalene	$C_{15}H_{24}$	263.0							
41	Diphenyl Methane	$(C_6H_5)_2CH_2$	265.0							
	Skatol	 $C_6H_4\left\langle {}^{NH}_{C(CH_3)} \right\rangle CH$	265–266							
24	Phenyl Acetic Acid	$C_6H_5CH_2CO_2H$	265.5					141.0		
103	n-Dodecyl Alcohol	$C_{12}H_{25}OH$					149.0	135.0		
40	Methyl Anthranilate	$C_6H_4(NH_2)CO_2CH_3$					141.0	124.0		
28	n-Capric Acid	$C_9H_{19}CO_2H$	268.4	202.0	184.8	173.5	165.0	152.0	141.3	135° 3 125° 1

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
38	n-Pentadecane	$C_{15}H_{32}$	270.5	194.0	173.0	160.0	150.0	135.0		
173	Phenyl Hexyl Ketone	$C_6H_5CO\ C_6H_{13}$	271.3				161.0	145.5		
24	Ethyl Cinnamate	$C_6H_5(CH)_2CO_2C_2H_5$	271.0					134.0		
	Dihydro Cumarine	$C_9H_8O_2$	272.0							
	Styrolene Glycol	$C_6H_5CH\ OH\ CH_2OH$	273.0							
105	Hexadecylene	$CH_2CH(CH_2)_{13}CH_3$	274.0				161.0	144.0		
40	Cadinene	$C_{15}H_{24}$	274.0						131.0	
106	Undecylenic Acid	$CH_2CH(CH_2)_8CO_2H$	275.0	213.5			171.0	159.0		
174	Propionyl Acetophenone	$C_6H_5CO\ CH_2COC_2H_5$	276–277			169–171				
24	Resorcine	$C_6H_4(OH)_2$	276.5				167.0	152.0		
24	as-Diphenyl Ethylene	$(C_6H_5)_2C\ CH_2$	277.0					135..		
24	m-Phenylen Diamine	$C_6H_4(NH_2)_2$	277.0					145.5		
24	Acenaphthene	$C_{10}H_6(CH)_2$	277.5				150.0	133.5		
38	Methyl Dodecyl Ketone	$C_{16}H_{25}CO\ CH_3$	278.0	206.0						
24	Diacetyl Resorcine	$C_6H_4(O\ CO\ CH_3)_2$	278.0				163.0	145.0		
168	Dioctyl	$C_8H_{17}C_8H_{17}$	278.0							
107	Eugenol Formate	$HCO_2C_6H_3(OCH_3)$-C_3H_5					150.0			
24	Ethyl Tartrate	$(CH\ OH\ CO_2C_2H_5)_2$	280.0					147.0		
24	m-Toluylene Diamine (1CH₃ : 2 : 4)	$C_6H_3CH_3(NH_2)_2$	280.0					151.0		
38	Undecylic Acid	$C_{10}H_{21}CO_2H$		212.5						
24	Ethyl-d-tartrate	$(CH\ OH\ CO_2C_2H_5)_2$	280.0					147.0		
175	n-Octyl Ethyl Ether	$C_8H_{17}O\ C_2H_5$	280–282							
28	α-Brom Naphthalene	$C_{10}H_7Br$	281.1	198.8	177.1	162.3	151.3	134.0	117.5	
109	Eugenol Acetate	$CH_3CO_2C_6H_3(OCH_3)$-C_3H_5						149.0	132.0	
24	Methyl Tartrate	$(CH\ OH\ CO_2CH_3)_2$	282.0					144.5		
24. 112	α-Naphthol	$C_{10}H_7OH$	282.5					143.0		
110	Hydrochinone	$C_6H_4(OH)_2$		216.7	196.0	183.9	175.1	162.8	152.0	
176	Dillapiol (1: 2: 3: 4: 5)	$C_6H(CH_2CH\ CH_2)(OCH_3)_2(O_2CH_2)$	285.0					159.5		
24, 100	Vanillin	$C_6H_3(CHO)(OCH_3)$-OH	285.0					155.0		
41	Phthalic Anhydride	$C_6H_4(CO)_2O$	286.0							
112	α-andβ-Thionaphthol	$C_{10}H_7SH$	286.0					134.0		
24	Benzyl Phenyl Ether	$C_6H_5CH_2OC_6H_5$	287.0					144.0		
24, 101	n-Glutaric-Anhydride	$CH_2(CH_2CO)_2O$	287.0					150.0		

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
24	Succinimide	$(CH_2CO)_2NH$	287.5					157.0		
38	n-Hexadecane	$C_{16}H_{34}$	287.5	208.5	187.5	174.0	165.0	149.0		
113	β-Naphthol	$C_{10}H_7OH$	288.0					146.0		80° 0.03
114	Guaiol (Sesquiterpene Alcohol)	$C_{15}H_{26}O$	288.0					148.0		
92	Tetradecyl Amine	$C_{14}H_{29}NH_2$					170.0	153.0		
24	Phthalide	$C_6H_4(CH_2)(CO)O$	290.0					144.0		
115	Glycerine	$C_3H_5(OH)_3$	290.0	220.1	203.5	191.8	182.2	167.2	155.5	118° 0.23
116	Myristicine	$C_6H_2(C_3H_5)(OCH_3)(O_2CH_2)$					158.0	142.0		
24	Cuminic Acid	$C_6H_4(C_3H_7)CO_2H$						160.0		
24	Cumarine	$C_9H_6O_2$	290.5					152.0		
177	Damascenine	$C_9H_{11}O_3N$						157.0		
170	Myristin Aldehyde	$C_{14}H_{28}O$		214–215			166–167			
117	Phenyl Sulphide	$(C_6H_5)_2S$	292.5				162.0	145.0		
38	Methyl Tridecyl Ketone	$C_{13}H_{27}CO\ CH_3$		219.0						
24	Ethyl Phthalate	$C_6H_4(CO_2C_2H_5)_2$	294.0					156.0		
24	Pyrogallol	$C_6H_3(OH)_3$						168.0		
118	Lauric Acid	$C_{11}H_{23}CO_2H$		227.5			181.0	167.0		
119	Fluoran	$(C_6H_4)_2CH_2$	295.0					147.0		
179	Methyl-α-naphthyl Ketone	$CH_3CO\ C_{10}H_7$	295–296					161–162		
	Asarone	$C_6H_2(OCH_3)_3C_3H_5$	296.0							
168	Octyl-n-Caprylate	$C_7H_{15}C\ O_2C_8H_{17}$	297–299							
24	Ditoyl Ethane	$C_2H_4(C_6H_4CH_3)_2$	298.0					154.0		
24	Ethyl-m-Nitrobenzoate	$C_6H_4NO_2CO_2C_2H_5$	298.0					155.0		
24	Cinnamic Acid	$C_6H_5(CH)_2CO_2H$	300.0					173.0		
24	α-Naphthyl Amine	$C_{10}H_7NH_2$	300.0					153.0		
24	Dibenzyl Amine	$(C_6H_5CH_2)_2NH$	300.0				181.0	163.0		
179	Methyl-β-Naphthyl Ketone	$CH_3CO\ C_{10}H_7$	300–301					168.5–169.5		
120	Octadecylene	$CH_2CH(CH_2)_{15}CH_3$					185.0	169.0		
121	β-Santalol	$C_{15}H_{24}O$	301.0					160.0		
24	Benzhydrol	$(C_6H_5)_2CH\ OH$	301.0					162.0		
24	Diphenyl Amine	$(C_6H_5)_2NH$	302.0					157.0		
123	n-Glutaric Acid	$CH_2(CH_2CO_2H)_2$	303.0					196.0		
38	n-Hepta Decane	$C_{17}H_{36}$	303.0	223.0	201.5	187.5	177.0	161.0		
24	Acetanilid	$CH_3CO\ NH\ C_6H_5$	303.8					162.0		

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
40	Menthyl Benzoate	$C_6H_5CO_2C_{10}H_{19}$					188.0	170.0		
124	Tridecylic Acid	$C_{12}H_{25}CO_2H$		236.0						
24	p-Methyl Stilbene	$C_6H_5(CH)_2C_6H_4CH_3$	304.0					175.0		
168	Octyl Benzoate	$C_6H_5CO_2C_8H_{17}$	305–306							
125	Benzophenone	$C_6H_5CO\ C_6H_5$	305.8					158.0		
179	Ethyl-α-Naphthyl Ketone	$C_2H_5CO\ C_{10}H_7$	305–307					170–172		
126	n-Tetradecyl Alcohol	$C_{14}H_{29}OH$	306.0				174.0	159.0		
24	Stilbene	$(C_6H_5CH)_2$	306.0					161.0		
38	Methyl Tetradecyl Ketone	$C_{14}H_{29}CO\ CH_3$	about 307.0	230.5						
127	β-Santalol	$C_{15}H_{25}O$	309.0					168.0		
117	Phenyl Disulphide	$(C_6H_5)_2S_2$	310.0				197.0	180.0		
24	p-Oxy Benzaldehyde	$C_6H_4(OH)CHO$	about 310.0							
179	i-Propyl-β-Naphthyl Ketone	$C_3H_7CO\ C_{10}H_7$	312–314					181.0		
24	Phenyl Salicylate (Salol)	$C_6H_4(OH)\ CO_2C_6H_5$	about 313.0					167.0		
24	Phenyl Benzoate	$C_6H_5CO_2C_6H_5$	314.0					158.0		
38	n-Octa Decane	$C_{18}H_{40}$	317.0		214.5	200.0	189.0	172.0		
24, 118	Myristinic Acid	$C_{13}H_{27}CO_2H$	about 318.0	250.0				187.0		
38	Methyl Pentadecyl Ketone	$C_{15}H_{31}CO\ CH_3$	319.0	242.0						
179	Isobutyl-α-Naphthyl Ketone	$C_4H_9CO\ C_{10}H_7$	319–321					183–185		
170	Palmitinic Aldehyde	$C_{16}H_{32}O$		239–240			190.0	105.0		
180	Phenyl Benzyl Ketone	$C_6H_5CO\ CH_2C_6H_5$	320–322					173.5		
181	Benzyl Benzoate	$C_6H_5CO_2CH_2C_6H_5$	323–324							
24	Isobutyl-d-Tartrate	$(CH\ OH\ CO_2C_4H_9)_2$	324.0					169.0		
38	Pentadecylic Acid	$C_{14}H_{29}CO_2H$		257.0						
128	Muskone	$C_{16}H_{30}O$						170.0	153.0	
131	Adipic Acid	$(CH_2)_4(CO_2H)_2$		165.0	244.5		223.0	205.5		
131	Pimelic Acid	$(CH_2)_5(CO_2H)_2$		272.0	251.5		231.0	212.0		
38	n-Nonadecane	$C_{19}H_{40}$	330.0	248.0	226.5	212.0	200.0	138.0		
129	Hexadecyl Amine	$C_{16}H_{33}NH_2$	330.0				194.0	177.0		
130	Dibenzyl Ketone	$(C_6H_5CH_2)_2CO$	330.5	246.6	224.5					
38	Methyl Hexadecyl Ketone	$CH_3COC_{16}H_{23}$		251.0						
24	Phenanthrene	$(C_6H_4CH)_2$	340.0					173.0		
132	Palmitinic Acid	$C_{15}H_{31}CO_2H$		271.5				207.0		
38	Methyl Heptadecyl Ketone	$CH_3COC_{17}H_{35}$		262.5						

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
133	n-Hexadecyl Alcohol (Cetyl Alcohol)	$C_{16}H_{33}OH$	344.0				196.0	179.0		
38	Margaric Acid	$C_{16}H_{33}CO_2H$		277.0						
38	n-Eicosan	$C_{20}H_{42}$					215.0	196.0		
182	Benzil	$(CO\ C_6H_5)_2$	346–348					183.0		
131	Suberic Acid	$C_8H_{14}O_4$		279.0	258.5		237.0	219.5		
	Benzyl Cinnamate	$C_6H_5(CH)_2CO_2CH_2C_6H_5$	350.0							
134	Geranyl Benzoate	$C_6H_5CO_2C_{10}H_{17}$						190.0		
135	Anthracene	$(C_6H_4CH)_2$	351.0	250.2	224.7	206.9	194.4	174.7	158.5	125° 1.0 111° 0.5 93° 0.2 81° 0.1 46° 0.01 16° 0.001 0° 0.00019
136	Triphenyl Methane	$(C_6H_5)_3CH$	353.0					197.0		
24	Diethyl Hexadecyl Amine	$C_{16}H_{33}N(C_2H_5)_2$	355.0							
137	Mercury	Hg	356.83	261.3	235.3	218.5	204.0	183.5	164.4	
183	Nitroglycerine	$C_3H_5(ONO_2)_3$								70° 0.051 18° 0.001
131	Azelaic Acid	$(CH_2)_7(CO_2H)_2$		286.5	265.0		244.0	225.5		
170	Stearic Aldehyde	$C_{18}H_{36}O$		259–261			210–212			
38	n-Heneicosan	$C_{21}H_{44}$	about 358.0				244.0	205.0		
24	Benzoic Anhydride	$(C_6H_5CO)_2O$	360.0					198.0		
138	Oleic Acid	$C_{17}H_{33}CO_2H$	about 360.0	286.0	264.0	249.5	240.0	223.0		
129	Elaidinic Acid	$C_{17}H_{33}CO_2H$	about 362.0	288.0	266.0	251.5	242.0	225.0		

TABLE II.—*Continued*

Lit. Ref.	Chemical compound	Chemical formula	760 mm.	100 mm.	50 mm.	30 mm.	20 mm.	10 mm.	5 mm.	Boiling temperatures under lower pressures
139	Stearic Acid	$C_{17}H_{35}CO_2H$	about 362.0	291.0				225.0		
38	n-Docosan	$C_{22}H_{46}$	about 370.0				232.0	213.0		
140	Anthrachinone	$(C_6H_4CO)_2$	377.0	286.2	268.4	256.4	247.7	233.0	218.0	
131	Sebacic Acid	$(CH_2)_8(CO_2H)_2$		294.5	273.0		251.0	232.0		
38	n-Tricosan	$C_{23}H_{48}$	about 383.0				242.0	223.0		
133	Octadecyl Alcohol	$C_{18}H_{37}OH$	about 384.0				220.0	202.0		
38	n-Tetracosan	$C_{24}H_{50}$	about 395.0					231.0		
101	Brassidic Acid	$C_{21}H_{41}CO_2H$				282.0	273.0	256.0		
184	Geranyl Palmitate	$C_{15}H_{31}CO_2C_{10}H_{17}$						256.0		
141	Sulphur	S_8	444.5	330.7	303.2			245.0		
38	n-Heptacosan	$C_{27}H_{56}$	about 430.0					270.5		
142	n-Dotriacontane	$C_{32}H_{66}$	about 485.0					310.5		
38	n-Penta Triacontane	$C_{35}H_{72}$	about 535.0					331.5		
143	Sodium	Na	742.0		563.6	559.4	540.6	507.4	471.6	
144	Cadmium	Cd	770.0	636.0	593.0	571.0	547.0			
144	Zinc	Zn	932.0	758.0	720.0	688.0	661.0			

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TABLE III.—BOILING POINT RELATIONS FOR VARIOUS BINARY MIXTURES

Component No. 1	Component No. 2	Miscibility at ordinary temperatures	Constant boiling mixtures	Boiling point of C.B.M. at 760 mm.	Weight per cent component No. 1 in C.B.M.	References
Acetaldehyde	Paraldehyde	Complete	None			1
Acetic Acid	Benzoic Acid					2
Acetic Acid	Benzene	Partial	Minimum	80.1°C.	2.0	3, 4, 5, 6
Acetic Acid	Benzophenone					2
Acetic Acid	Butyric Acid					7
Acetic Acid	Carbon Bisulphide	Complete	None			8
Acetic Acid	Diphenyl Amine					2
Acetic Acid	Meta Xylene	Complete	Minimum	114.0°C.	27.0	8
Acetic Acid	Picoline	Complete	Maximum	146.5°	about 50.0	9
Acetic Acid	Picric Acid					2
Acetic Acid	Pyridine	Complete	Maximum			10, 11, 12
Acetic Acid	Salicylic Acid					2
Acetic Acid	Toluene	Complete	Minimum	104.0°	30.0	5, 8, 12
Acetic Acid	Triethyl Amine	Complete	Maximum	162.0°	31.3	11
Acetic Acid	Trimethyl Amine	Complete	Maximum			9
Acetic Acid	Water	Complete	None			3, 13, 7, 14, 15
Acetone	Benzoic Acid					2
Acetone	Benzene	Complete	None			16, 17, 18
Acetone	Carbon Bisulphide	Complete	Minimum	39.25°	34.0	8, 19, 20 21
Acetone	Carbon Tetrachloride	Complete	Minimum			22
Acetone	Chloroform	Complete	Maximum	64.7°	80.0	12, 8, 22 19, 20, 21, 23, 24
Acetone	Diethyl Amine	Complete	Minimum	51.3°	38.2	25
Acetone	Ethyl Benzoate					2
Acetone	Ethyl Acetate	Complete	None			8
Acetone	Ethyl Alcohol	Complete	None			22, 24
Acetone	Ethyl Bromide	Complete	None			8
Acetone	Ethyl Ether	Complete	None			2, 22, 8, 27
Acetone	Ethyl Iodide	Complete	Minimum	55.5°	60.0	8, 12
Acetone	Methyl Acetate	Complete	Minimum	55.5°		8
Acetone	Methyl Alcohol	Complete	Minimum	55.95°	86.5	22, 28, 8
Acetone	Methyl Ethyl Ketone	Complete	None			29
Acetone	Phenol	Complete	None			30
Acetone	Propyl Bromide	Complete	None			
Acetone	Nitroglycerine	Complete	None			25
Acetone	Water	Complete	None			32, 22, 30, 33
Acetylene	Ethane	Complete	Minimum			34, 35, 36
Allyl Alcohol	Benzene	Complete	Minimum	76.5°	20.0	8
Allyl Alcohol	Toluene	Complete	Minimum	91.5°	50.0	8
Allyl Alcohol	Water	Complete	Minimum			37
Ammonia	Ethyl Alcohol	Complete	None			38
Ammonia	Isobutyl Alcohol	Complete	None			38
Ammonia	Propyl Alcohol	Complete	None			38
Ammonia	Water	Complete	None			39, 40, 15, 42
Amyl Acetate	Amyl Alcohol	Complete	Minimum	129.1°	2.6	43
Amyl Acetate	Amyl Bromide	Complete	None			43
Amyl Acetate	Amyl Iodide	Complete	None			43
Amyl Acetate	Bromoform	Complete	None			43
Amyl Acetate	Ethylene Bromide	Complete	None			43
Amyl Alcohol	Amyl Bromide	Complete	Minimum	116.15°	12.7	43
Amyl Alcohol	Benzene	Complete	None			19, 20
Amyl Alcohol	Brombenzene	Complete	None			8
Amyl Alcohol	Bromoform	Complete	None			43
Amyl Alcohol	Ethane	Complete				44, 45

TABLE III.—*Continued*

Component No. 1	Component No. 2	Miscibility at ordinary temperatures	Constant boiling mixtures	Boiling point of C.B.M. at 760 mm.	Weight per cent component No. 1 in C.B.M.	References
Amyl Alcohol	Ethyl Butyrate	Complete	None			43
Amyl Alcohol	Ethylene Bromide	Complete	Minimum	121.5°	30.0	8
Amyl Alcohol	Hexane	Complete	None			19, 20
Amyl Alcohol	Isobutyl Iodide	Complete	Minimum	115.5°	20.0	8
Amyl Alcohol	Propyl Bromide	Complete	None			31
Amyl Alcohol	Toluene	Complete	None			8
Amyl Alcohol	Water	Partial				3, 14, 46, 25
Amyl Alcohol	Xylenes	Complete	Minimum	125°–128°	52.0	8
Amyl Bromide	Ethyl Alcohol	Complete	Minimum			31
Amyl Bromide	Ethyl Butyrate	Complete	None			43
Amyl Bromide	Isobutyl Alcohol	Complete	Minimum	103.4°	36.4	43
Amyl Bromide	Methyl Alcohol	Complete	Minimum			31
Amyl Bromide	Propyl Alcohol	Complete	Minimum			43
Amyl Bromide	Toluene	Complete	None			43
Amyl Iodide	Isobutyl Alcohol	Complete	None			43
Amyl Iodide	Propyl Alcohol	Complete	Minimum			43, 47
Amyl Valerate	Water	Partial				46
Amylene	Aniline	Partial				48
Amylene	Ethyl Alcohol	Complete	None			49
Amylene	Nitrobenzene	Complete	None			48
Amylene	Turpentine					2
Amylene	Thymol					2
Amylene	Valerianic Acid					2
Aniline	Carbon Bisulphide					2
Aniline	Ethyl Ether	Complete	None			50, 51
Aniline	Water	Partial				52, 53
Benzene	Benzoic Acid					2
Benzene	Brombenzene	Complete	None			5
Benzene	Carbon Bisulphide	Complete	None			54, 32, 55, 56, 57, 58
Benzene	Carbon Tetra-Chloride	Complete	Minimum			56, 59, 60, 5, 61, 19, 20, 12, 31
Benzene	Chlorbenzene	Complete	None			5
Benzene	Chloroform	Complete	None			56, 5, 8
Benzene	Diphenyl Amine					2
Benzene	Ethyl Acetate	Complete	Minimum			59, 60, 8
Benzene	Ethyl Alcohol	Complete	Minimum	68.25°	67.6	56, 59, 60, 57, 8, 61, 62, 19, 20
Benzene	Ethyl Benzoate					2
Benzene	Ethyl Bromide	Complete	None			55
Benzene	Ethyl Ether	Complete	None			56
Benzene	Ethyl Iodide	Complete	None			8
Benzene	Ethylene Chloride	Complete	None			12, 21
Benzene	Hexane	Complete	Minimum			63
Benzene	Isobutyl Alcohol	Complete	Minimum	79.85°	90.7	8, 19, 20
Benzene	Isopropyl Alcohol	Complete	Minimum	71.9°	66.7	8, 19, 20
Benzene	Methyl Acetate	Complete	None			59, 60
Benzene	Methyl Alcohol	Complete	Minimum	58.35°	60.5	56, 8, 19, 20
Benzene	Naphthalene					2
Benzene	Nitrobenzene					2
Benzene	Propyl Alcohol	Complete	Minimum	77.1°	83.1	8, 19, 20
Benzene	Tertiary Butyl Alcohol	Complete	Minimum	73.95°	63.4	19, 20
Benzene	Toluene	Complete	None			19, 20
Benzene	Water	Partial				64, 57, 19
Benzoic Acid	Ethyl Bromide					2
Brombenzene	Butyric Acid	Complete	Minimum	148.0°	81.0	8

TABLE III.—*Continued*

Component No. 1	Component No. 2	Miscibility at ordinary temperatures	Constant boiling mixtures	Boiling point of C.B.M. at 760 mm.	Weight per cent component No. 1 in C.B.M.	References
Brombenzene	Chlorbenzene	Complete	None			19, 20
Brombenzene	Toluene	Complete	None			5
Bromine	Water	Partial				65
Bromoform	Butyric Acid	Complete	Minimum			31
Butyl Alcohol	Carbon Bisulphide	Partial				66
Butyl Alcohol	Ethane	Partial				44, 45
Butyl Alcohol	Water	Partial				3
Butyl Butyrate	Water	Partial				46
Butyl Iodide	Water	Partial				67
Butyric Acid	Water	Partial	Minimum	99.0°	68.0	3, 14, 37, 8
Caprylic Acid	Water	Partial				3
Carbon Bisulphide	Camphor					2
Carbon Bisulphide	Carbon Dioxide	Complete	None			68
Carbon Bisulphide	Carbon Tetrachloride	Complete	None			69, 70, 57
Carbon Bisulphide	Chloroform	Partial	Minimum			49
Carbon Bisulphide	Ethyl Acetate	Complete	Minimum	45.0°	92.0	8, 70
Carbon Bisulphide	Ethyl Alcohol	Partial	Minimum	42.0°	91.0	71, 69, 70, 72, 49, 66, 8
Carbon Bisulphide	Ethyl Benzoate					2
Carbon Bisulphide	Ethyl Bromide	Complete	Minimum	37.0°	68.0	8
Carbon Bisulphide	Ethyl Ether	Complete	Minimum	34.5	41.0	71, 55, 49, 57, 8, 19, 20
Carbon Bisulphide	Ethyl Iodide	Complete	Minimum			8
Carbon Bisulphide	Isopropyl Alcohol	Complete	Minimum	44.0°	91.0	8
Carbon Bisulphide	Methyl Acetate	Complete	Minimum	40.0°	71.0	8
Carbon Bisulphide	Methyl Alcohol	Partial				8, 73
Carbon Bisulphide	Methylal	Complete	Minimum	37.25°	60.0	19, 20, 12
Carbon Bisulphide	Naphthalene					2
Carbon Bisulphide	Nitrobenzene					2
Carbon Bisulphide	Perchlorethane	Complete	None			2, 57
Carbon Bisulphide	Propyl Alcohol	Partial				66
Carbon Bisulphide	Thymol					2
Carbon Bisulphide	Turpentine					2
Carbon Bisulphide	Valerianic Acid					2
Carbon Bisulphide	Water	Partial				57, 64
Carbon Dioxide	Chloroform	Complete	None			68
Carbon Dioxide	Ethane	Complete	Minimum			59, 60, 36, 23
Carbon Dioxide	Hydrochloric Acid	Complete	None			74
Carbon Dioxide	Methyl Chloride	Complete	None			75, 76, 77, 78
Carbon Dioxide	Sulphur Dioxide	Complete	None			75
Carbon Dioxide	Sulphuric Acid	Complete	None			79, 80
Carbon Dioxide	Water	Partial	None			44, 45, 80
Carbon Tetrachloride	Chlorbenzene	Complete	None			81
Carbon Tetrachloride	Chloroform	Complete	None			22
Carbon Tetrachloride	Ethyl Acetate	Complete	Minimum	74.8°		19, 20, 82
Carbon Tetrachloride	Ethyl Alcohol	Complete	Minimum	64.9°	84.0	22, 61
Carbon Tetrachloride	Ethyl Iodide	Complete	Minimum			12
Carbon Tetrachloride	Methyl Alcohol	Complete	Minimum	55.7°	79.4	56, 54, 19, 20
Carbon tetrachloride	Nitrobenzene	Complete	None			5

TABLE III.—*Continued*

Component No. 1	Component No. 2	Miscibility at ordinary temperatures	Constant boiling mixtures	Boiling point of C.B.M. at 760 mm.	Weight per cent component No. 1 in C.B.M.	References
Carbon Tetrachloride	Propyl Alcohol	Complete	Minimum			31
Carbon Tetrachloride	Toluene	Complete	None			59, 60, 5, 31
Chloral	Water	Complete	Minimum	95.0°	93.0	83
Chlorbenzene	Toluene	Complete	None			5
Chlorbenzene	Water	Partial				19
Chlorine	Water	Partial				65, 84
Chloroform	Ethyl Acetate	Complete	None			8
Chloroform	Ethyl Alcohol	Complete	Minimum	59.0°	94.0	8, 22, 24
Chloroform	Ethyl Benzoate					2
Chloroform	Ethyl Bromide	Complete	None			8
Chloroform	Ethyl Ether	Complete	None			55, 49, 56, 81, 8
Chloroform	Ethyl Iodide	Complete	None			8
Chloroform	Isopropyl Alcohol	Complete	None			8
Chloroform	Methyl Acetate	Complete	Maximum	64.5°	22.0	8
Chloroform	Methyl Alcohol	Complete	Minimum	54.0°	89.0	8, 22, 28
Chloroform	Toluene	Complete	None			56, 5
m-Cresol	o-Cresol	Complete	None			85
Cresol {o m p}	Phenol	Complete	None			85
Diphenyl Amine	Ethyl Alcohol					2
Ethane	Ethyl Alcohol	Partial				44, 45
Ethane	Hydrochloric Acid	Complete	Minimum			86
Ethane	Isopropyl Alcohol	Partial				44, 45
Ethane	Methyl Alcohol	Partial				44, 45, 66
Ethane	Nitrous Oxide	Complete	Minimum			34, 35, 36
Ethane	Propyl Alcohol	Partial				44, 45
Ethane	Water	Partial				44, 45
Ethyl Acetate	Ethyl Alcohol	Complete	Minimum	71.0°	69.0	8
Ethyl Acetate	Ethyl Butyrate	Complete	None			43
Ethyl Acetate	Ethyl Iodide	Complete	Minimum	70.0°	22.0	12
Ethyl Acetate	Ethyl Propionate	Complete	None			19, 20
Ethyl Acetate	Isopropyl Alcohol	Complete	Minimum	74.0°	74.0	8
Ethyl Acetate	Methyl Alcohol	Complete	Minimum	62.0°	53.0	8
Ethyl Acetate	Propyl Alcohol	Complete	None			8
Ethyl Alcohol	Ethyl Benzoate					2
Ethyl Alcohol	Ethyl Bromide	Complete	Minimum	37.0°	3.0	8
Ethyl Alcohol	Ethyl Ether	Complete	None			22, 28, 87, 88
Ethyl Alcohol	Ethyl Iodide	Complete	Minimum	63.0	14.0	8
Ethyl Alcohol	Hexane	Partial	Minimum			19, 20, 66
Ethyl Alcohol	Isobutyl Bromide	Complete	Minimum			31
Ethyl Alcohol	Isobutyl Iodide	Complete	Minimum	77.0°	70.0	8
Ethyl Alcohol	Methyl Alcohol	Complete	None			56, 19, 20, 89
Ethyl Alcohol	Methyl Cyanide	Complete	Minimum	72.6°	55.0	90
Ethyl Alcohol	Methyl Ethyl Ketone	Complete	Minimum	75.0°		25
Ethyl Alcohol	Naphthalene					2
Ethyl Alcohol	Nitrobenzene					2
Ethyl Alcohol	Picric Acid					2
Ethyl Alcohol	Propyl Alcohol	Complete	None			8
Ethyl Alcohol	Propyl Bromide	Complete	Minimum			31
Ethyl Alcohol	Resorcine	Complete	None			91
Ethyl Alcohol	Thymol					2
Ethyl Alcohol	Toluene	Complete	Minimum	76.7°		19, 20, 59, 60
Ethyl Alcohol	Water	Complete	Minimum	78.15°	95.57	71, 69, 92, 93, 3, 22, 14, 94, 95, 15, 19, 96, 97

TABLE III.—*Continued*

Component No. 1	Component No. 2	Miscibility at ordinary temperatures	Constant boiling mixtures	Boiling point of C.B.M. at 760 mm.	Weight per cent component No. 1 in C.B.M.	References
Ethyl Benzoate	Ethyl Bromide					2
Ethyl Benzoate	Ethyl Ether	Complete	None			50, 98, 65
Ethyl Benzoate	Water	Partial				64
Ethyl Benzene	Toluene	Complete	None			19, 20
Ethyl Bromide	Ethyl Iodide	Complete	None			49
Ethyl Bromide	Methyl Alcohol	Complete	Minimum	35.0°	95.0	8
Ethyl Bromide	Water	Partial				64
Ethyl Ether	Methyl Alcohol	Complete	None			8, 56, 28
Ethyl Ether	Methyl Salicylate	Complete	None			2, 65
Ethyl Ether	Nitrobenzene	Complete	None			50, 98, 65, 48
Ethyl Ether	Turpentine	Complete	None			50, 98, 65
Ethyl Ether	Water	Partial				44, 6, 57, 47, 25
Ethyl Iodide	Isobutyl Alcohol	Complete	None			8
Ethyl Iodide	Isopropyl Alcohol	Complete	Minimum	66.0°	87.0	8
Ethyl Iodide	Methyl Alcohol	Complete	Minimum	55.0°	83.0	8, 54, 42
Ethyl Iodide	Propyl Alcohol	Complete	Minimum	70.0°	93.0	8
Ethyl Iodide	Water	Partial				67
Ethylene Bromide	Isobutyl Alcohol	Complete	Minimum	105.0°	38.0	8
Ethylene Bromide	m-Xylene	Complete	None			8
Ethylene Bromide	Propylene Bromide	Complete	None			12
Formic Acid	Picoline	Complete	Maximum	156°–159°		11
Formic Acid	Pyridine	Complete	Maximum	149.0°		11, 10
Formic Acid	Trimethyl Amine	Complete	Maximum			9
Formic Acid	Water	Complete	Maximum	107.1°	77.0	99, 3, 13, 7, 14, 37, 100, 101, 102
Glycerine	Water	Complete	None			
Hexane	Isobutyl Alcohol	Complete	Minimum	68.1°		19, 20
Hexane	Methyl Alcohol	Partial	Minimum	50.0°		8, 66
Hexane	Nitrobenzene	Complete	None			
Hexane	Octane	Complete	None			19, 20
Hexane	Propyl Alcohol	Complete	Minimum	65.65°		19, 20
Hydrazine	Water	Complete	Maximum	119.0°		104
Hydriodic Acid	Water	Complete	Maximum	127.0°	57.0	100, 101, 105
Hydrobromic Acid	Water	Partial	Maximum	126.0°	47.5	99, 65, 100, 101, 105
Hydrochloric Acid	Methyl Ether	Complete	Maximum	−2°C.	61.0	114, 115
Hydrochloric Acid	Water	Partial	Maximum	110.0°	21.2	106, 99, 108, 109, 110, 15, 65, 105, 111
Hydrofluoric Acid	Water	Complete	Maximum	120.0°	37.0	112, 113
Hydrogen Sulphide	Water	Partial				84
Isobutyl Acetate	Isobutyl Alcohol	Complete	None			31
Isobutyl Alcohol	Isobutyl Bromide	Complete	None			31
Isobutyl Alcohol	m-Xylene	Complete	None			8
Isobutyl Alcohol	Propyl Alcohol	Complete	None			8
Isobutyl Alcohol	Propyl Bromide	Complete	None			31
Isobutyl Alcohol	Toluene	Complete	Minimum	100.0°	43.0	8
Isobutyl Alcohol	Water	Partial	Minimum			19, 14, 67
Isobutyl Bromide	Methyl Alcohol	Complete	Minimum			31
Isobutyl Bromide	Propyl Alcohol	Complete	Minimum			31
Isobutyl Iodide	Isobutyl Alcohol	Complete	Minimum	101.0°		8
Isobutyl Iodide	Isopropyl Alcohol	Complete	Minimum	81.0°	30.0	8
Isobutyl Iodide	Methyl Alcohol	Complete	Minimum	64.0°	30.0	8
Isobutyl Iodide	Propyl Alcohol	Complete	Minimum	92.5°	55.0	8
Isobutyl Iodide	Toluene	Complete	None			8

TABLE III.—*Continued*

Component No. 1	Component No. 2	Miscibility at ordinary temperatures	Constant boiling mixtures	Boiling point of C.B.M. at 760 mm.	Weight per cent component No. 1 in C.B.M.	References
Isopropyl Alcohol	Toluene	Complete	None			8
Isopropyl Alcohol	Water	Complete	Minimum	80.35°	87.9	8, 116, 117
Methyl Acetate	Methyl Alcohol	Complete	Minimum	54.0°	82.0	8, 43
Methyl Acetate	Water	Partial				25
Methyl Alcohol	Methyl Cyanide	Complete	Minimum	63.7°	77.0	90
Methyl Alcohol	Methyl Iodide	Complete	Minimum			31
Methyl Alcohol	Methyl Salicylate					98
Methyl Alcohol	Pentane	Partial	Minimum			66
Methyl Alcohol	Propyl Bromide	Complete	Minimum			31
Methyl Alcohol	Thymol					2
Methyl Alcohol	Propane	Partial	Minimum			66
Methyl Alcohol	Toluene	Complete	None			8
Methyl Alcohol	Water	Complete	None			3, 119, 22, 14, 96, 97
Methyl Chloride	Sulphur Dioxide		Maximum Minimum			120
Methyl Ethyl Ketone	Water	Partial				25
Methyl Iodide	Nitrobenzene	Complete	None			48
Naphthalene	Water	Partial				64
Nitrobenzene	Water	Partial				64
Nitrobenzene	Pentane	Partial				48
Nitrogen	Oxygen	Complete	None			121, 122
Perchloric Acid	Water	Complete	Maximum	203.0°	71.6	123
Phenol	Water	Partial	Minimum			124, 52, 53
Propionic Acid	Water	Complete	None			14
Propionic Acid	Pyridine	Complete	Maximum	149.0°		10, 11
Propyl Alcohol	Propyl Bromide	Complete	Minimum			31
Propyl Alcohol	Toluene	Complete	Minimum	91.0°	53.0	8
Propyl Alcohol	Water	Complete	Minimum	87.7°	71.7	125, 3, 4, 13, 22, 14, 23, 8, 126, 127, 19, 97
Propyl Propionate	Water	Partial				46
Pyridine	Water					128, 12
Sulphur	Toluene	Partial				129
Sulphur	Xylene	Partial				129
Sulphur Dioxide	Water	Partial				65, 84
Sulphuric Acid	Water	Complete	Maximum			130, 131, 132, 133, 15, 134, 135
Turpentine	Water	Partial				64
Tertiary Butyl Alcohol	Water	Complete	Minimum			19, 136
Toluene	Water	Partial				64, 19
Triethyl Amine	Water	Partial	Minimum			66, 49, 137
Trimethyl Pyridine	Water	Partial	Minimum			137
Xylene	Water	Partial				64

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Table IV.—Steam Distillation of Various Substances
(From Rechenberg)

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
Acetic Acid..	CH_3CO_2H	60.0	118.7	37.0	46.7 29.3	38.3	67.4	6
		60.0		88.0	487.0 273.0	35.4	64.6	
		60.0		129.18	1981.0 1059.0	33.8	63.0	
Acetephenone	$C_6H_5CO\ CH_3$	120.0	201.5	45.9	74.7 1.32	1.72	10.4	14
		120.0		99.05	734.6 25.8	3.30	18.5	
		120.0		142.32	2901.4 138.3	4.31	23.1	
Amyl Butyrate	$C_3H_7CO_2C_5H_{11}$	158.0	178.6	97.87	703.0 56.2	7.19	40.5	18
		158.0		140.83	2782.0 258.0	8.08	43.5	
AmylFormate	$HCO_2C_5H_{11}$	116.0	123.3	36.55	45.5 30.5	39.8	81.0	18
		116.0		89.1	508.0 252.0	32.3	75.7	
		116.0		131.0	2092.0 948.0	30.1	73.5	
Amyl Propionate	$C_2H_5CO_2C_5H_{11}$	144.0	160.2	43.8	67.0 9.0	11.7	51.5	18
		144.0		96.25	663.9 96.1	12.3	52.9	
		144.0		138.77	2642.0 415.7	13.7	54.6	
Aniline......	$C_6H_5NH_2$	93.0	183.9	45.9	74.75 1.56	2.02	9.64	14
		93.0		98.4	717.7 43.0	5.50	23.1	
		93.0		141.3	2819.5 219.0	6.87	27.4	
Benzaldehyde	C_6H_5CHO	106.0	178.3	45.3	72.5 3.6	4.70	22.5	14
		106.0		97.9	706.0 56.5	7.21	31.4	
		106.0		140.7	2772.0 268.0	9.50	38.2	
Benzene.....	C_6H_6	78.0	80.2	16.0	13.5 62.5	82.3	95.3	15
		78.0		69.2	225.0 535.0	70.0	91.0	
		78.0		112.6	1173.0 1867.0	60.4	86.9	
Benzoic Acid.	$C_6H_5CO_2H$	122.0	249.0	143.78	3021.9 17.6	0.56	3.65	14
Benzonitril...	C_6H_5CN	103.0	190.6	45.7	74.0 2.08	2.72	13.8	14
		103.0		98.5	720.4 40.0	5.12	23.6	
		103.0		141.55	2839.4 201.0	6.25	27.7	
Benzyl Alcohol	$C_6H_5CH_2OH$	108.0	205.0	99.4	744.0 14.58	1.87	10.2	14
		108.0		142.7	2932.4 106.5	3.32	17.1	
Brombenzene	C_6H_5Br	157.0	155.5	43.0	64.31 11.8	15.3	61.3	14
		157.0		95.1	636.1 123.2	15.9	62.2	
		157.0		137.9	2559.7 481.3	15.1	60.9	

TABLE IV.—*Continued*

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
α-Bromnaphthaline	$C_{10}H_7Br$	207.0	281 1	99.9	757.33 2.27	0.290	3.24	14
		207.0		143.8	2023.6 14.94	0.545	5.09	
n-Butyl Alcohol	C_4H_9OH	74.0	117.6	40.6	56.7 19.0	25.1	58.0	14
		74.0		89.4	513.7 247.0	31.9	65.8	
n-Butyric Acid	$C_3H_7CO_2H$	88.0	160.0	45.2	72.1 3.9	5.09	20.8	24
		88.0		97.5	694.4 66.0	8.4	31.0	
		88.0		139.7	2695.0 343.0	10.8	37.1	
Camphor....	$C_{10}H_{16}O$	152.0	206.0	46.0	75.13 0.98^{26}	1.27	9.82	
		152.0		99.08	735.4 24.57^{27}	3.14	21.5	
		152.0		142.6	2924.0 117.0^{27}	3.41	24.2	
n-Caprinic Acid	$C_9H_{19}CO_2H$	172.0	268.4	143.93	3034.4 5.97	0.185	1.74	14
n-Caproic Acid	$C_4H_{11}CO_2H$	116.0	205.7	99.6	749.3 10.26	1.32	7.93	14
n-Caprylic Acid	$C_7H_{15}CO_2H$	142.0	237.5	99.9	757.33 1.58	0.202	1.57	14
		142.0		143.65	3011.1 29.08	0.903	6.71	
Carbon Bisulphde...	CS_2	76.12	46.0	−11.5	1.784 74.09	97.6	99.4	5
		76.12		43.27	65.24 694.85	91.3	97.8	
		76.12		88.13	489.3 2550.4	82.7	95.3	
Chinoline...	C_9H_7N	129.0	237.8	99.7	752.0 8.4	1.08	7.28	28
		129.0		143.4	2990.0 52.2	1.62	10.6	
m-Chlor Aniline	$C_6H_4ClNH_2$	127.45	228.5	99.68	751.4 8.85	1.13	7.49	14
		127.45		143.27	2979.4 60.06	2.16	13.5	
o-Chlor Aniline	$C_6H_4ClNH_2$	127.45	208.8	99.25	740.0 20.05	2.64	16.1	14
		127.45		142.63	2926.7 113.4	3.53	20.6	
Chlor Naphthalene	$C_{10}H_7Cl$	162.45	259.3	99.85	756.0 3.87	0.496	4.30	14
		162.45		143.65	3011.1 28.38	0.882	7.43	
m-Cresol.....	$C_6H_4(CH_3)OH$	108.0	200.5	99.3	741.3 18.0	2.30	12.4	14
		108.0		142.54	2919.3 120.6	3.76	19.0	
o-Cresol....	$C_6H_4(CH_3)OH$	108.0	190.1	45.8	74.38 1.64	2.16	11.7	14
		108.0		98.84	729.14 30.0	3.83	19.3	
		108.0		141.95	2871.0 171.3	5.34	25.3	
p-Cresol.....	$C_6H_4(CH_3)OH$	108.0	201.1	99.35	742.6 17.6	2.25	12.1	14
		108.0		142.56	2921.0 118.9	3.70	18.7	
Diethyl Aniline.....	$C_6H_5N(C_2H_5)_2$	149.0	215.5	99.5	746.7 24.2	1.81	13.3	14
		149.0		142.96	2953.5 86.7	2.70	18.7	

TABLE IV.—*Continued*

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
Diisobutyl...	C_8H_{18}	114.0	109.2	31.6	34.6 41.65	54.5	88.4	7
		114.0		83.7	411.6 346.9	45.2	83.9	
		114.0		126.5	1825.3 1214.4	38.8	80.1	
Diisopropyl..	C_6H_{14}	86.0	58.08	−1.3	4.21 71.9	94.7	98.4	7
		86.0		53.4	108.8 651.1	85.2	96.5	
		86.0		98.35	716.4 2323.0	75.9	93.8	
Dimethyl Aniline.....	$C_6H_5N(CH_3)_2$	151.0	193.1	46.0	75.13 1.69	2.17	15.7	14
		151.0		98.7	725.5 33.4	4.28	27.3	
		151.0		141.85	2863.6 176.7	5.44	32.5	
Dimethyl-o-Toluidine ..	$C_6H_4(CH_3)N(CH_3)$	135.0	184.8	45.5	73.25 2.78	3.66	22.0	14
		135.0		98.3	715.1 45.6	5.82	31.7	
		135.0		141.3	2819.4 220.8	7.64	38.3	
Dimethyl-p-Toluidine ..	$C_6H_4(CH_3)N(CH_3)_2$	135.0	209.5	99.3	741.3 19.0	2.43	15.7	14
		135.0		142.56	2921.0 109.0	3.41	20.9	
Ethyl Acetate	$CH_3CO_2C_2H_5$	88.0	77.15	17.0	14.4 61.5	80.9	95.4	1
		88.0		67.5	209.2 551.8	71.9	92.6	
		88.0		109.6	1061.0 1976.0	64.3	89.8	
Ethyl Alcohol	C_2H_5OH	46.0	78.3	23.75	21.8 54.2[14]	70.2	86.4	
		46.0		69.2	225.4 534.6[12]	69.9	85.6	
		46.0		106.1	942.0 2098.0[12]	68.2	84.6	
Ethyl Aniline	$C_6H_5NHC_2H_5$	121.0	204.0	99.9	757.3 2.2	3.29	18.6	14
		121.0		142.5	2916.1 124.6	3.88	21.34	
Ethyl Ether..	$(C_2H_5)_2O$	74.0	34.61	−17.23	1.1 75.0[2]	98.4	99.6	
		74.0		32.7	36.8 723.2[2]	94.8	98.7	
		74.0		76.25	304.3 2735.5[2]	89.8	97.3	
Ethyl Formate	$HCO_2C_2H_5$	74.0	54.3	0°	4.60 72.45	94.1	98.5	
		74.0		50.7	95.3 664.8	87.3	96.6	
		74.0		92.8	584.0 2457.0	80.4	94.4	
Ethyl Isobutyrate ...	$C_3H_7CO_2C_2H_5$	116.0	110.1	32.7	36.8 39.2	51.4	87.2	18
		116.0		84.5	424.7 335.3	46.8	85.0	
		116.0		126.8	1826.0 1214.0	38.7	80.3	
Ethyl Propionate	$C_2H_5CO_2C_2H_5$	102.0	99.0	29.2	30.1 45.9	61.2	89.9	1
		102.0		80.0	354.9 403.6	52.6	86.3	
		102.0		121.8	1578.6 1462.8	47.0	83.4	

TABLE IV.—*Continued*

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
Formic Acid.	HCO_2H	46.0	100.75	27.8	27.75 48.5^{14}	63.4	81.6	
		46.0		81.35	374.8 385.2^{20}	50.1	72.0	
Glycerine....	$C_3H_5(OH)_3$	92.0	290.0	143.96	3036.9 3.00	0.093	0.475	29
n-Heptane...	C_7H_{16}	100.0	98.43	26.8	26.17 50.35	64.6	91.3	19
		100.0		79.15	342.9 417.3	54.4	86.9	
		100.0		122.06	1591.5 1448.8	46.6	82.9	
n-Heptylic Acid	$C_6H_{13}CO_2H$	130.0	221.0	99.9	757.7 4.27	0.51	3.71	14
		130.0		143.5	2998.6 50.4	1.56	10.3	
Hexamethylene..	C_6H_{12}	84.0	80.85	15.8	13.3 62.8	82.6	95.7	16
		84.0		69.5	228.4 532.7	69.0	91.3	
		84.0		113.3	1200.0 1840.0	59.6	87.3	
n-Hexane	C_6H_{14}	86.0	69.0	7.7	7.83 68.1	89.5	97.7	10
		86.0		61.55	160.0 600.4	78.6	94.6	
		86.0		105.43	920.1 2119.4	68.9	91.4	
Iodobenzene.	C_6H_5I	203.85	188.2	45.2	72.1 3.8	4.97	37.2	25
		203.85		98.2	712.5 47.4	6.06	42.2	
		203.85		141.4	2827.5 214.0	6.68	44.8	
Isoamyl Alcohol....	$C_5H_{11}OH$	88.0	130.1	43.0	64.3 11.7	15.2	46.8	21
		88.0		92.7	581.9 176.0	22.7	59.0	
		88.0		132.9	2210.0 831.0	26.3	63.5	
Isobutyl Acetate....	$CH_3CO_2C_4H_9$	116.0	116.3	36.15	44.5 31.5	41.4	81.9	18
		116.0		87.9	484.9 275.1	36.5	78.1	
		116.0		128.75	1954.5 1085.5	34.4	77.2	
Isobutyl Alcohol...	C_4H_9OH	74.0	107.92	38.1	49.7 26.3	34.5	68.4	20
		74.0		85.5	441.8 318.2	42.1	74.9	
Isobutyl Butyrate	$C_3H_7CO_2C_4H_9$	144.0	156.9	95.9	654.8 105.2	13.5	55.5	18
		144.0		138.35	2593.0 447.0	16.4	56.7	
Isobutyl Formate	$HCO_2C_4H_9$	102.0	97.9	28.5	29.0 47.0	61.9	90.2	18
		102.0		79.0	340.7 419.3	54.5	87.2	
		102.0		121.1	1544.0 1496.0	44.9	84.0	
Isobutyric Acid.......	$C_3H_7CO_2H$	88.0	153.3	44.2	68.5 7.1	9.32	33.4	21
		88.0		96.25	663.7 96.1	12.0	40.7	
		88.0		138.2	2582.0 459.0	14.4	45.2	

TABLE IV.—*Continued*

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
Isocaproic Acid	$(CH_3)_2CHCH_2CH_2CO_2H$	116.0	200.5	99.5	746.7 12.7	1.62	9.61	14
		116.0		142.7	2932.6 107.0	3.33	18.2	
Mercury.....	Hg	200.0	356.83	46.22	75.99[30] 0.0105	0.014	0.16	
		200.0		99.99	759.72[30] 0.284	0.036	0.40	
		200.0		143.97	3037.79[31] 2.206	0.073	0.80	
Methyl Acetate	$CH_3CO_2CH_3$	74.0	57.1	2.05	5.30 70.6	93.0	98.2	1
		74.0		53.3	108.3 652.0	85.7	96.1	
		74.0		94.5	623.0 2417.0	79.1	94.0	
Methyl Alcohol	CH_3OH	32.0	64.7	12.5	10.8 65.2	85.8	91.5	8
		32.0		59.5	145.5 614.5	80.6	88.1	
		32.0		96.8	677.0 2363.0	77.4	85.9	
Methyl Aniline	$C_6H_5NHCH_3$	107.0	193.8	99.0	733.3 27.25	3.48	17.7	14
		107.0		142.1	2883.5 157.1	4.90	23.4	
Methyl Benzoate	$C_6H_5CO_2CH_3$	136.0	197.5	46.0	75.13 1.39	1.80	12.15	14
		136.0		98.95	732.0 28.06	3.58	21.9	
		136.0		142.2	1891.6 148.5	4.60	26.7	
Methyl Butyrate	$C_3H_7CO_2CH_3$	102.0	102.75	30.6	32.6 43.3	56.9	88.2	1
		102.0		81.6	378.6 382.0	49.6	84.8	
		102.0		123.4	1660.0 1375.0	44.2	81.8	
Methyl Formate	HCO_2CH_3	60.0	31.8	−18.2	1.1 74.0	98.3	99.5	1
		60.0		30.65	32.7 727.6	95.8	98.7	
		60.0		71.42	248.1 2791.6	91.8	97.4	
Methyl Isobutyrate	$C_3H_7CO_2CH_3$	102.0	92.3	25.0	23.5 52.2	69.0	92.7	1
		102.0		76.5	307.5 452.5	59.1	89.1	
		102.0		118.7	1609.0 1431.0	49.0	84.5	
Methyl Propionate	$C_2H_5CO_2CH_3$	88.0	79.7	18.2	15.5 60.6	79.6	95.0	1
		88.0		69.2	225.4 534.6	76.7	94.2	
		88.0		111.2	1117.6 1921.8	62.3	89.0	
Naphthaline	$C_{10}H_8$	128.0	218.1	46.08	75.4 0.565	0.735	5.0	26
		128.0		99.33	741.8 18.1	2.31	14.4	
Nitrobenzene	$C_6H_5NO_2$	123.0	208.3	99.25	740.0 20.15	2.58	15.2	14
		123.0		142.65	2928.3 110.5	3.44	19.6	
o-Nitrotoluene	$C_6H_4(CH_3)NO_2$	137.0	220.4	99.55	748.0 12.5	1.63	11.2	14
		137.0		143.07	2962.7 77.3	2.72	15.8	

TABLE IV.—*Continued*

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
p-Nitrotoluene	$C_6H_4(CH_3)NO_2$	137.0	237.7	99.7	752.0 7.38	0.955	6.82	14
		137.0		143.4	2990.22 48.63	1.51	10.5	
n-Octane.....	C_8H_{18}	114.0	125.8	37.8	48.7 27.4	35.6	77.8	11
		114.0		89.3	511.5 248.0	32.0	74.9	
		114.0		131.7	2136.0 902.4	28.9	71.8	
n-Pelargic Acid	$C_8H_{17}CO_2H$	156.0	253.4	99.99	759.73 0.28	0.036	0.31	14
		156.0		143.8	3023.6 15.06	0.468	3.91	
n-Pentane....	C_5H_{12}	72.0	36.3	−18.2	1.1 75.0	98.4	99.6	4
		72.0		34.6	40.9 719.0	94.6	98.6	
		72.0		79.35	345.7 2695.0	88.3	96.8	
Phenol.......	C_6H_5OH	94.0	181.4	46.0	75.13 1.18	1.53	7.50	14
		94.0		98.6	722.9 37.8	4.81	20.9	
		94.0		141.4	2827.5 214.0	6.68	27.2	
Propionic Acid	$C_2H_5CO_2H$	74.0	140.3	43.3	65.4 10.9	14.2	40.4	23
		74.0		94.3	617.6 142.5	18.3	48.0	
		74.0		135.6	2395.0 645.0	20.4	51.3	
Propyl Acetate	$CH_3CO_2C_3H_7$	102.0	101.55	30.3	32.1 43.9	57.7	88.6	1
		102.0		81.1	371.0 389.5	50.6	85.3	
		102.0		122.95	1636.4 1404.5	45.1	82.3	
n-Propyl Alcohol	C_3H_7OH	60.0	97.4	33.8	39.0 37.0	48.4	75.8	17
		60.0		80.9	368.0 392.0	51.0	77.6	
		60.0		118.7	1431.0 1609.0	51.8	78.2	
Propyl Formate	$HCO_2C_3H_7$	88.0	80.9	18.7	16.03 59.9	78.8	94.8	1
		88.0		70.1	244.6 526.0	68.8	91.5	
		88.0		112.15	1155.7 1883.0	61.1	88.5	
Propylene Bromide	$CH_3CHBrCH_2Br$	202.0	141.0	41.0	57.87 18.4	25.0	78.9	14
		202.0		92.9	586.2 173.1	22.4	76.4	
		202.0		135.55	2392.2 647.4	20.5	74.3	
Sulphur......	S_8		440.0	100.0	760.0 0.007		0.013	32
Toluene......	$C_6H_5CH_3$	92.0	110.4	32.0	35.32 40.8	53.3	85.4	14
		92.0		84.45	421.6 338.5	43.9	80.0	
m-Toluidine..	$C_6H_4(CH_3)NH_2$	107.0	203.3	99.22	739.2 20.8	2.66	14.0	14
		107.0		142.5	2916.1 124.0	3.88	19.4	

Table IV.—*Continued*

Substance	Formula	Mol weight of substance	Boiling point at 760 mm. pressure	Temperature of steam distillation	Partial pressure of the components upper-water lower substance	Mol per cent of substances in vapor	Weight per cent of substances in vapor	References
o-Toluidine	$C_6H_4(CH_3)NH_2$	107.0	199.7	46.0	75.13 0.89	1.16	6.51	14
		107.0		99.1	736.0 24.4	3.12	16.1	
		107.0		142.3	2899.8 139.1	4.34	21.2	
p-Toluidine	$C_6H_4(CH_3)NH_2$	107.0	200.4	99.1	736.0 23.6	3.01	15.6	14
		107.0		142.35	2903.8 136.3	4.25	20.9	
Trimethylene Bromide	$CH_2BrCH_2BrCH_2$	202.0	164.4	96.5	669.7 90.1	11.6	59.4	14
		202.0		139.31	2665.1 375.1	11.8	60.0	
n-Valerianic Acid	$C_4H_9CO_2H$	102.0	184.4	99.0	733.3 27.5	3.54	17.1	14
		102.0		141.9	2867.3 175.0	5.45	24.6	
p-Xylene	$C_6H_4(CH_3)_2$	106.0	138.45	92.2	571.0 188.0	24.3	65.3	22

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TABLE V.—TABLE OF LATENT HEATS OF VAPORIZATION

Substance	Boiling point, degrees, Centigrade	Molecular weight	Latent heat in calories per gram at boiling point
Acetal	104.0	118.1	66.2
Acetaldehyde	20.8	44.0	134.6
Acetic Acid	118.7	60.0	89.8
Acetic Anhydride	136.4	102.1	66.1
Acetone	56.6	58.1	125.3
Acetyl Chloride	55.6	78.5	78.9
Ammonia	– 34.7	17.0	341.0
Aniline	183.9	93.1	109.6
Benzaldehyde	178.3	106.1	86.6
Benzene	80.2	78.1	93.5
Benzyl Alcohol	205.0	108.1	98.5
Brombenzene	155.5	157.0	57.9
Butyl Alcohol (n)	117.6	74.1	143.3
Butyl Alcohol (iso)	107.9	74.1	138.9
Butyric Acid (iso)	162.2	88.1	114.0
Carbon Tetrachloride	76.8	153.8	46.4
Chlorbenzene	131.8	112.5	75.9
Chloroform	61.2	119.4	58.9
Cresol (m)	200.5	108.1	100.5
Ethyl Bromide	38.2	109.0	60.4
Ethyl Iodide	72.3	155.9	47.6
Formic Acid	100.8	46.0	120.4
Glycol	197.1	62.1	190.9
Heptane	98.4	100.2	74.0
Hexane	69.0	86.1	79.2
Iso amyl Alcohol	130.1	88.1	125.1
Iso propyl Alcohol	82.9	60.1	161.1
Methyl Alcohol	64.7	32.0	261.7
Methyl Chloride	– 24.1	50.5	96.9 (at 0°C.)
Methyl Iodide	42.4	141.9	46.0
Methyl Ethyl Ketone	81.0	72.1	103.5
Octane	125.8	114.2	71.1
Methyl Aniline	193.8	107.1	95.5
Nitrobenzene	208.3	123.1	79.2 (at 151.5°C.)
Pentane	36.3	72.1	85.8
Propyl Alcohol (n)	97.4	60.1	162.6
Toluene	110.4	92.1	86.8
o-Toluidene	203.3	107.1	95.1
o-Xylene	144.0	106.1	82.5
Water	100.0	18.0	536.6

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